

Synthesis of Vanadium Oxide Gels from Peroxovanadic Acid Solutions: A ⁵¹V NMR Study

Bruno Alonso and Jacques Livage

Chimie de la Matière Condensée, Université Pierre et Marie Curie, Paris, France

Received March 2, 1999; accepted March 16, 1999

Vanadium pentoxide gels are formed via the reaction of V₂O₅ powder with hydrogen peroxide. ⁵¹V NMR studies of the solution show that the dissolution of the oxide leads to the formation of solute diperoxo [VO(O₂)₂]⁻ species. These peroxy species are not stable in the solution. They progressively decompose giving monoperoxo [VO(O₂)₂]⁺ and then vanadate species. Oxygen gas evolves and a solution of decavanadic acid [H_nV₁₀O₂₈]⁽⁶⁻ⁿ⁾⁻ is formed after few hours. The decavanadic acid then spontaneously dissociates giving rise to the polymerization of V₂O₅.nH₂O gels similar to those currently synthesized via the acidification of vanadate aqueous solutions. These gels exhibit a liquid crystal behavior and give rise to strongly oriented vanadium oxide coatings when deposited onto a flat substrate. © 1999 Academic Press

Key Words: V₂O₅ gels; peroxovanadates; ⁵¹V NMR; sol-gel.

INTRODUCTION

Vanadium pentoxide gels V₂O₅.nH₂O have been extensively studied for their electronic and ionic properties. They can be used as antistatic coatings for photographic films or reversible cathode for lithium batteries (1). Such gels are currently prepared via the acidification of vanadate NaVO₃ aqueous solutions (2) or the hydrolysis and condensation of vanadium alkoxides (3). They exhibit a layered structure made of double V₂O₅ sheets and behave as a versatile host structure for the intercalation of ionic and molecular species (1, 4). The formation of such gels from aqueous solutions was followed by ⁵¹V and ¹⁷O NMR showing that decavanadic acid [H₂V₁₀O₂₈]⁴⁻ and dioxovanadium cations [VO₂]⁺ behave as precursors for the formation of the vanadium oxide (5, 6).

At the beginning of the century Düllberg showed that vanadium oxide gels could also be obtained via the reaction of V₂O₅ with H₂O₂ (7). A similar procedure was recently developed by Kudo using metallic vanadium instead of V₂O₅. According to the authors, a new vanadium oxide was obtained that exhibits a two-dimensional structure based on a three-fold lamella built up from the *a-b* planes of orthorhombic V₂O₅ (8). This 2D vanadium oxide exhibits promis-

ing properties as a cathode material for lithium batteries or electrochromic devices (9). The dissolution of solid precursors (oxide or metal) into hydrogen peroxide solutions is a commonly used process for the wet synthesis of transition metal oxides such as WO₃, MoO₃, or TiO₂ (10–12). It is supposed that such solutions contain solute peroxy species but the chemical processes leading to the precipitation of oxides or peroxides is not well described. Therefore this paper presents a ⁵¹V NMR analysis of the formation of V₂O₅.nH₂O gels from aqueous solutions of peroxy vanadic acid.

EXPERIMENTAL

Synthesis of V₂O₅.nH₂O Gels

The dissolution reaction of V₂O₅ in H₂O₂ is highly exothermic and can even be very violent when concentrated hydrogen peroxide solutions are used (30%). A gelatinous flocculate is then readily formed within a few minutes that appears mainly amorphous by X-ray diffraction. More diluted H₂O₂ solutions have then been used in order to be able to control the formation of the gel. The V₂O₅ powder (1 g) is dissolved in a hydrogen peroxide solution (100 ml, 10%). An exothermic reaction occurs during which hydrogen peroxide is partially decomposed leading to the release of oxygen gas. A clear orange solution is formed after about 10 min (final pH 1.5). O₂ still evolves slowly from the solution that turns deep red after about 2 h. Then oxygen bubbling progressively stops, the color turns orange-yellow, and a red-brown gelatinous flocculate forms after a few hours. This flocculate swells spontaneously in the yellow mother solution giving rise to a homogeneous viscous dark red gel about 24 h later. Upon drying in air under ambient conditions this gel leads to a V₂O₅.nH₂O xerogel (*n* ≈ 2). The X-ray diffraction pattern of such xerogels deposited onto a flat substrate exhibits a series of 00*l* peaks typical of some preferred orientation of a layered structure (Fig. 1). The basal distance deduced from the position of these peaks, *d* ≈ 12 Å, is close to that observed for V₂O₅.1.8H₂O xerogels obtained via the acidification of metavanadate aqueous solutions (13, 14).

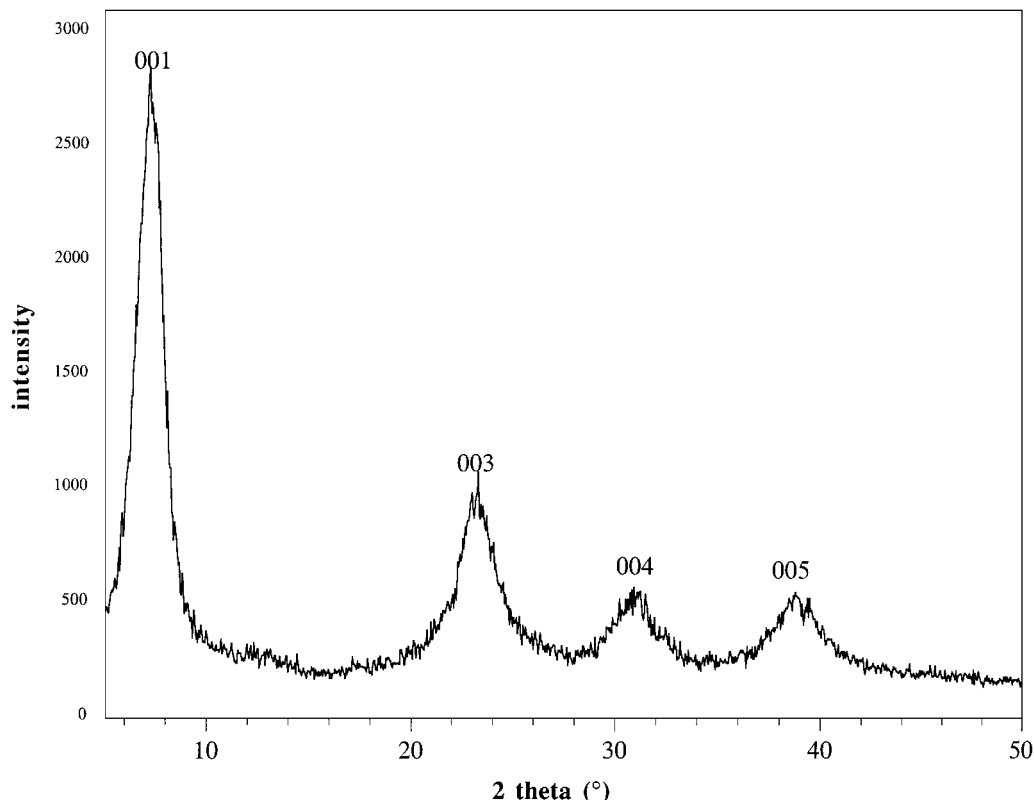


FIG 1. X-ray diffraction pattern of a $V_2O_5 \cdot 2H_2O$ layer deposited from a vanadium oxide gel.

⁵¹V NMR of Peroxovanadate Solutions

⁵¹V NMR solution spectra were recorded on a Bruker AM250 spectrometer operating at 65.7 MHz, using a 90° pulse width of 16 μs, a relaxation delay of 1 s, and a spectral linewidth of 62.5 kHz. Neat VOCl₃ is used as an external reference for chemical shifts ($\delta = 0$ ppm). All spectra are recorded with the same sample in order to be able to make quantitative measurements.

The ⁵¹V NMR spectrum of the orange solution obtained just after dissolution exhibits a single sharp peak around $\delta = -695$ ppm (Fig. 2a) that can be assigned to the orange diperoxo anion $[VO(O_2)_2]^-$ (15–17). This peak progressively broadens and decreases in intensity with time while oxygen gas evolves from the solution. It moves slightly downfield ($\delta = -691$ ppm) and a small bump appears around $\delta = -670$ ppm (Fig. 2c). The origin of this peak is not clear. It has previously been attributed to $[V_2O(O_2)_4(H_2O)_2]$ dimeric species and is only observed in the presence of an excess of H₂O₂ (18).

The solution turns red after 200 min and four new peaks appear while the peak due to the diperoxo species progressively disappears (Fig. 2d). The three peaks at $\delta \approx -530$, -510 , and -425 ppm are typical of the diprotonated decavanadate species $[H_2V_{10}O_{28}]^{4-}$ (19). The red coloration

of the solution suggests that the small peak around $\delta \approx -539$ ppm should correspond to the red oxoperoxo cation $[VO(O_2)]^+$ (20, 21). The red coloration and the peak at $\delta = -539$ ppm progressively disappear within about 1 h while another small peak grows around $\delta = -545$ ppm. (Fig. 2e) This should be due to the $[VO_2]^+$ cation which is the stable form of V^V below pH ≈ 2 (22). Only oxo species $[VO_2]^+$ and $[H_2V_{10}O_{28}]^{4-}$ are observed after 270 min before gelation occurs (Fig. 2f).

The ⁵¹V NMR spectrum of the solution then progressively decreases in intensity as gelation continues. This should be due to the condensation of molecular precursors giving rise to a vanadium oxide network. Quantitative measurements based on the surface of ⁵¹V NMR peaks show that the total amount of vanadium seen by NMR remains constant over a large period of time (≈ 4 h). The surface of the peak corresponding to the diperoxo species $[VO(O_2)_2]^-$ decreases rapidly after 175 min while the surface of the signal due to decavanadic acid begins to grow (Fig. 3). The amount of decavanadic acid decreases rapidly after 4 h and no signal can be observed any longer by solution ⁵¹V NMR after 6 h MAS NMR experiments have then been performed on these gels. They give a NMR signal similar to that observed already with $V_2O_5 \cdot nH_2O$ gels synthesized from aqueous solutions.

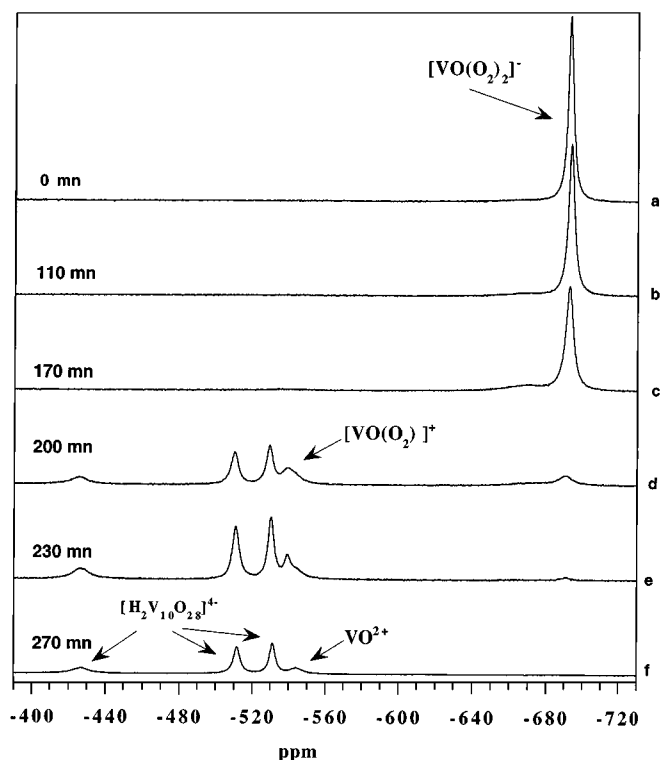


FIG 2. Evolution of the ^{51}V NMR spectra of peroxovanadate solutions as a function of time.

DISCUSSION

Hydrogen peroxide is able to coordinate to V^{V} in aqueous solution forming peroxo complexes (21). The well-known spot test for vanadate, for instance, is based on the

formation of the red peroxovanadium ion. Both the red monoperoxo $[\text{VO}(\text{O}_2)]^+$ and the yellow diperoxo $[\text{VO}(\text{O}_2)_2]^-$ species are actually observed at low pH. V^{V} is six-fold coordinated and peroxo groups are bound in the equatorial plane relative to the $\text{V}=\text{O}$ double bond.

We may then assume that the dissolution of V_2O_5 powders in hydrogen peroxide leads to the formation of solute peroxo species such as those already described in the literature. However these peroxo species slowly decompose and the formation of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels can be described as follows:

V_2O_5 dissolves in the presence of an excess of hydrogen peroxide giving an orange solution of diperoxo anions $[\text{VO}(\text{O}_2)_2]^-$. The H_2O_2 solution is highly acidic ($\text{pH} \approx 0$) and the pH of the resulting solution is very low ($\text{pH} \approx 1.5$). Peroxovanadate species appear to be unstable in these solutions. Hydrogen peroxide in excess and peroxo groups are slowly oxidized giving oxygen gas. Monoperoxo and oxo V^{V} species are then progressively formed as peroxo groups are decomposed. No free hydrogen peroxide can be detected in the solution after 3 h and an aqueous solution of $[\text{VO}_2]^+$ and $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ is finally obtained.

Such solutions are similar to those obtained via the acidification of metavanadates through proton exchange resins (1, 5). The pH is about the same ($\text{pH} \approx 1.5$) and the solution should behave the same way, giving rise to $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels as described previously (23). We have shown that such solutions spontaneously polymerize to give ribbon-like vanadium oxide particles. A similar mechanism should be involved here. Upon aging, the solution becomes progressively more viscous and a dark red gel is formed. Vanadium oxide gels synthesized from peroxo solutions

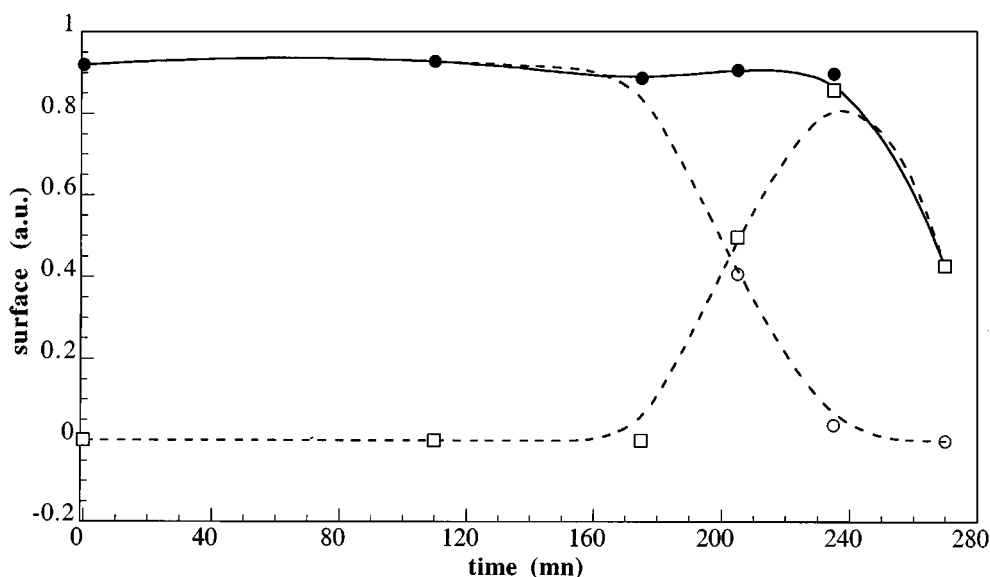


FIG 3. V^{V} species distribution as a function of time, deduced from the surface of ^{51}V NMR peaks. (black circles) total amount of vanadium, (white circles) peroxo species $[\text{VO}(\text{O}_2)_2]^-$ and $[\text{VO}(\text{O}_2)]^+$, (white squares) vanadates species $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ and VO_2^+ .

should then have a layered structure close to that of $V_2O_5 \cdot nH_2O$ gels obtained via the condensation of vanadic acid. When deposited onto a flat substrate, these gels give thick films that exhibit some preferred orientation. Their X-ray diffraction pattern observed in reflection geometry exhibits a series of 00l harmonics typical of the turbostratic stacking of V_2O_5 ribbons. Moreover the 002 peak cannot be observed suggesting that the structure of peroxovanadic gels is similar to that of polyvanadic acid gels, i.e., formed of double sheets of V_2O_5 (4, 14). When observed by optical microscopy through crossed polarizers, they exhibit defects typical of nematic liquid crystals like aqueous vanadium oxide gels and sols (24, 25).

The peroxy route is very easy to perform. One of its main advantages would be to avoid the presence of foreign ions such as Na^+ that often remain in the gel even after ion exchange. The concentration of vanadium in $V_2O_5 \cdot nH_2O$ sols and gels can also be accurately controlled. It only depends on the volume of H_2O_2 solution added to the V_2O_5 powder. This is not the case with the ion exchange process in which additional water included in the resin has to be taken into account. The concentration of vanadic acid solutions is not constant. They are highly diluted at the beginning of ion exchange and much more concentrated at the end. With H_2O_2 , the viscosity of vanadium oxide sols can be accurately adjusted to the deposition process (spin-coating or dip-coating) when thin films have to be made.

Peroxy ions $[O_2]^{2-}$ are currently used to control the formation of transition metal oxides from aqueous solutions (10–12). They behave as chelating bidentate ligands. They prevent condensation reactions and avoid the precipitation of the oxide. Tungstic acid aqueous solutions, for instance, can be formed via the acidification of tungstate solutions. However they are not stable and a crystalline precipitate of $WO_3 \cdot 2H_2O$ is formed within a few hours (26). The condensation of polytungstic species can be chemically controlled by adding H_2O_2 . Peroxopolytungstic acids are formed in which chelating $[O_2]^{2-}$ ligands prevent the formation of the oxide network. Such solutions are very stable and can be conveniently used for the deposition of electrochromic thin films (27,28). Hydrogen peroxide in excess and peroxopolytungstic species are not decomposed and hydrated tungsten peroxides $[WO_2(O_2)H_2O] \cdot nH_2O$ can be crystallized from such solution (29). It has to be pointed out that aqueous solutions of peroxovanadates are not so stable. They spontaneously lead to the formation of $V_2O_5 \cdot nH_2O$ gels rather than peroxy compounds. This should be due to

the catalytic properties of V^V that favor the decomposition of peroxy complexes allowing condensation reactions to proceed. Adding hydrogen peroxide then only slows down condensation but does not lead to a new vanadium oxide.

REFERENCES

1. J. Livage, *Chem. Mater.* **3**, 578 (1991).
2. N. Gharbi, C. Sanchez, J. Livage, J. Lemerle, and J. Lefebvre, *J. Inorg. Chem.* **21**, 2758 (1982).
3. C. Sanchez, M. Nabavi, and F. Taulelle, *Mater Res. Soc. Symp. Proc.* **121**, 93 (1988).
4. T. Yao, Y. Oka, and N. Yamamoto, *Mater Res. Bull.* **27**, 669 (1992).
5. G. A. Pozarnsky, and A. V. McCornick, *Chem. Mater.* **6**, 380 (1994).
6. G. A. Pozarnsky, and A. V. McCornick, *J. Mater. Chem.* **4**, 1749 (1994).
7. P. Düllberg, *Z. Phys. Chem.* **45**, 129 (1903)
8. M. Hibino, U. Ugaji, A. Kishimoto, and T. Kudo, *Solid State Ionics* **79**, 239 (1995).
9. M. Ugaji, M. Hibino, and T. Kudo, *J. Electrochem. Soc.* **142**, 3664 (1995).
10. T. Kudo, H. Okamoto, K. Matsumoto, and Y. Sasaki, *Inorg. Chim. Acta* **111**, L27 (1986).
11. A. Aoki, and G. Nogami, *J. Electrochem. Soc.* **143**, L191 (1996).
12. K. Hinokuma, K. Ogasawara, A. Kishimoto, and T. Kudo, *Solid State Ionics* **53–56**, 507 (1992).
13. P. Aldebert, N. Baffier, N. Gharbi, and J. Livage, *Mater. Res. Bull.* **16**, 669 (1981).
14. J. J. Legendre, P. Aldebert, N. Baffier, and J. Livage, *J. Colloid Interface Sci.* **94**, 84 (1983).
15. N. J. Campbell, A. C. Dengel, and W. P. Griffith, *Polyhedron* **8**, 1379 (1989).
16. V. Conte, F. Di Furia, and S. Moro, *J. Mol. Catal.* **94**, 323 (1994).
17. C. Slebodnick, and V. L. Pecoraro, *Inorg. Chim. Acta* **283**, 37 (1998).
18. O. W. Howarth, and J. R. Hunt, *J. Chem. Soc. Dalton Trans.* 1388 (1979).
19. O. W. Howard, and M. J. Jarrold, *J. Chem. Soc., Dalton Trans.* 503 (1978).
20. A. T. Harrison, and O. W. Howarth, *J. Chem. Soc. Dalton Trans.* 1173 (1985).
21. A. Butler, M. J. Clague, and G. E. Meister, *Chem. Rev.* **94**, 625 (1994).
22. M. T. Pope, "Hetero and Isopoly Oxometallates, Inorganic Chemistry Concepts," Vol. 8. Springer-Verlag, Berlin, 1983.
23. J. Livage, *Coord. Chem. Rev.* **178–180**, 999 (1998).
24. P. Davidson, A. Garreau, and J. Livage, *Liquid Crystals* **16**, 905 (1994).
25. P. Davidson, private communication.
26. A. Chemseddine, R. Morineau, and J. Livage, *J. Solid State Ionics* **9–10**, 357 (1983).
27. K. Yamanaka, H. Oakamoto, H. Kidou, and T. Kudo, *Jpn. J. Appl. Phys.* **25**, 1420 (1986).
28. B. Pecquenard, H. Lecacheux, S. Castro-Garcia, and J. Livage, *J. Sol-Gel Sci. Technol.* **13**, 923 (1998).
29. B. Pecquenard, S. Castro-Garcia, J. Livage, P. Y. Zavalij, M. S. Whittingham, and R. Thouvenot, *Chem. Mater.* **10**, 1882 (1998).