



Local Structure of Nanoscopic Materials: V_2O_5 Nanorods and Nanowires

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Abstract

Divanadium pentoxide (γ - V_2O_5) nanorods and nanowires have been synthesized by reverse micelle technique. The length can be tuned easily by keeping the particles in micellar solution after the synthesis from 40 nm to 1 μ m. The local structure of these nanocrystals has been studied by high resolution transmission electron microscopy, Fourier transform infrared spectroscopy and electron energy loss spectroscopy. The results obtained demonstrate that a combination of experimental and theoretical tools permit to accurately characterize the local structure of nanomaterials.

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In order to understand the catalytic properties of a compound it is important to know its local structure. The study of local structures of nanosized materials is, however, rather challenging seeing that crystallographic studies and surface characterization of nanophase materials are difficult to perform.

The present letter demonstrates that this task can be fulfilled by a combination of experimental and theoretical tools.

Vanadium oxide based catalysts are widely used in a variety of chemical reactions like partial oxidation of alkanes or selective reduction of NO_x [1].

In the past decade vanadium pentoxide gels have been extensively studied [2], more recently Nesper et al. [3–5] found a way to synthesize vanadium oxide nanotubes ($\text{VO}_x\text{-NT}_s$) by sol-gel reaction of a vanadium alkoxide with a primary amine or a α,ω -diamine, followed by a hydrothermal treatment. Niederberger et al. [6] synthesized mixed valent vanadium oxide nanorods via a nonaqueous low temperature procedure.

In a previous publication a new soft chemical way to synthesize divanadium pentoxide (V_2O_5) nanorods by using the reverse micelle technique was presented [7]. It was shown that it is possible to control the size of the nanorods simply by keeping the particles in micellar solution up from several hours to a few days. Here we study two samples aged respectively of 24 hours and 100 days. The average length of the nanorods are 90 nm and $1\mu\text{m}$ for the nanowires. In order to study the catalytic activity of these nanoobjects it is important to know their geometric and electronic structure. It is of great interest to prepare geometrically well-defined V^{5+} radicals as physical vapour deposition methods give no access to thin films or clusters model catalysts of this catalytically relevant oxidation state.

Divanadium pentoxide nanorods and nanowires have been synthesized by colloidal self assembly made of sodium bis(ethyl-2-hexyl)sulfosuccinate $\text{Na}(\text{AOT})/\text{Isooctane}/\text{H}_2\text{O}$ [7]. The water content (w) defined as the ratio of water to surfactant concentrations $w = \frac{[\text{H}_2\text{O}]}{[\text{AOT}]}$ is kept constant $w = 10$. Under such experimental conditions reverse micelles are formed. A solution of the alkoxide $\text{VO}(\text{OR})_3$ with $\text{R}=\text{CH}(\text{CH}_3)_2$, in isooctane is then rapidly added to the micellar solution. The nanocrystals are formed instantaneously. The solution takes a brown color. The alkoxide concentration is kept constant at $[\text{VO}(\text{OR})_3]= 5 \cdot 10^{-3}\text{M}$. After 24 hours or 100 days one drop of this solution is then deposited on a carbon film. In the figure 1 A and C typical

transmission electron micrographs of the particles aged of 24 hours and 100 days respectively are shown [8]. The high resolution images (Figure 1 B and D) reveal lattice fringes of the nanocrystals. The lattice fringes are in good agreement with the γ - V_2O_5 structure for the nanorod oriented in the $[101]$ direction (Fig 1 B) and for the nanowire oriented in the $[100]$ direction (Fig 1 D). The nanocrystals show a good crystallinity even without any thermal treatment.

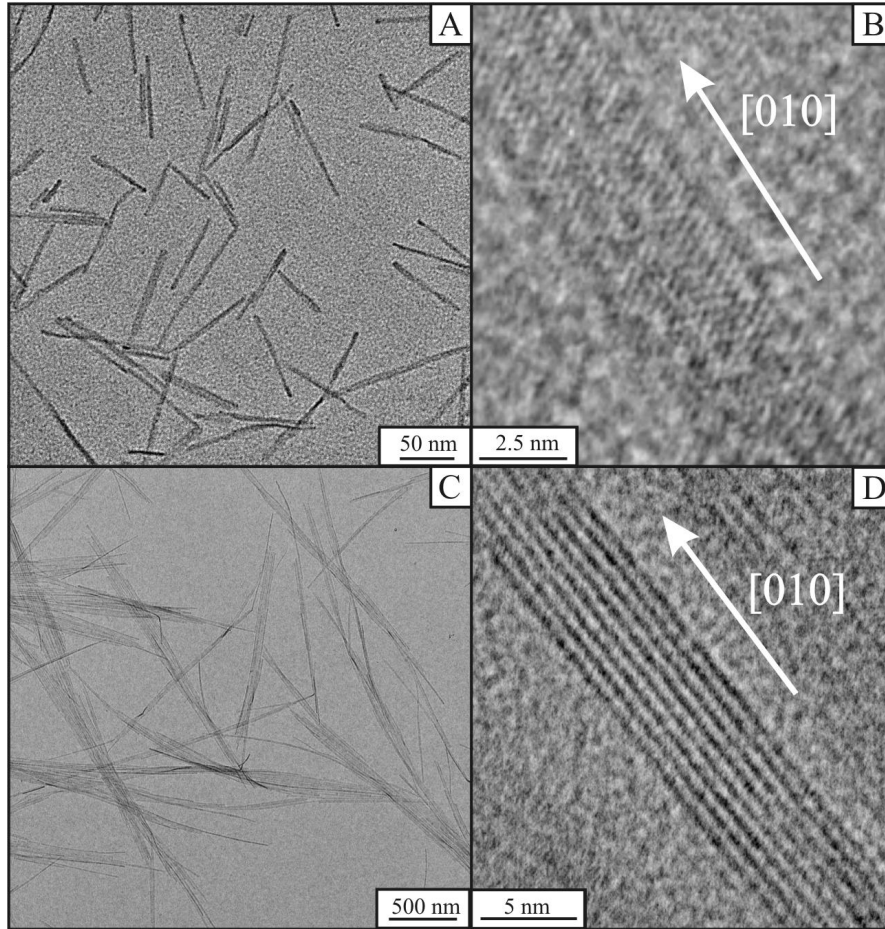


Figure 1: Vanadium oxide nanocrystals synthesized in reverse micelles observed after 24 hours (A) and 100 days (C) in micellar solution, high resolution transmission electron microscopy of a part of a nanorod oriented in the $[101]$ direction (B) and nanowire oriented in $[100]$ direction (D)

V_2O_5 crystallizes in two structures; the most common α - V_2O_5 (Fig. 2 top) and the γ - V_2O_5 (Fig. 2 bottom) [9]. The γ - V_2O_5 forms a layer type orthorhombic lattice with lattice constants $a = 9.946 \text{ \AA}$, $b = 3.585 \text{ \AA}$ and $c = 10.042 \text{ \AA}$. The structure is set up by layers of edge and

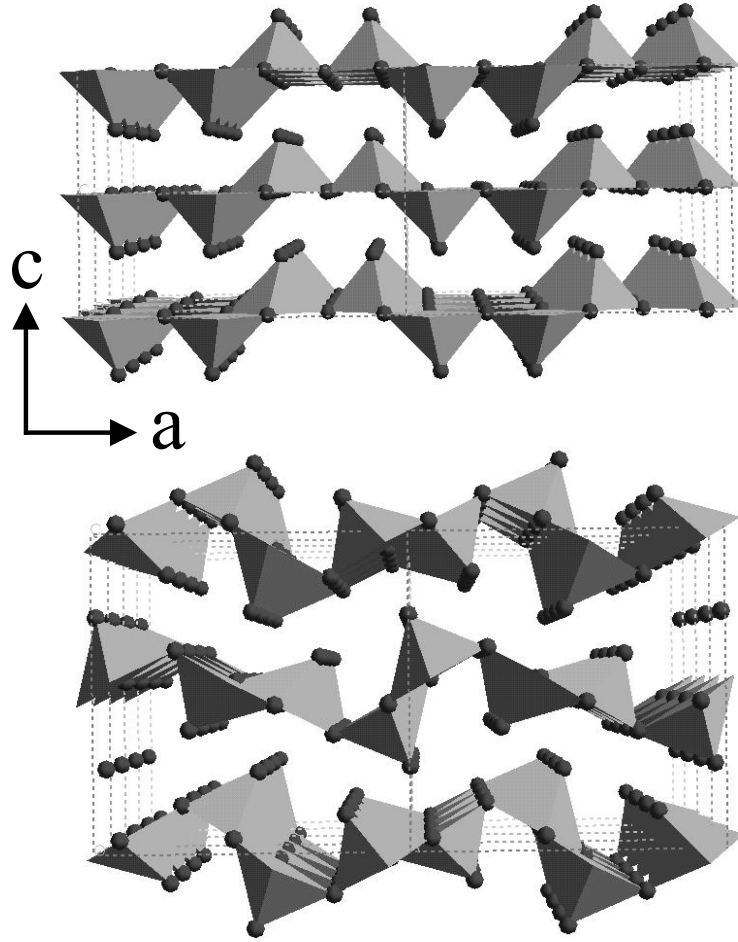


Figure 2: Representation of the two possible V_2O_5 structures: α - V_2O_5 (top) and γ - V_2O_5 (bottom)

corner sharing VO_5 pyramids sticking out at both sides of the layer. As opposed to α - V_2O_5 , where all vanadyl bonds are oriented along c , the double chains of edge sharing pyramids in γ - V_2O_5 are tilted relatively to each other. As a consequence, there exist two structurally different VO_5 pyramids. The first site can also be thought of as a bi-pyramidal (VO_6) by including the weak interlayer bond to the vanadyl oxygen of the adjacent layer. The second site is a VO_5 pyramid positioned in such a way that no oxygen atom lies in close vicinity of the basal plane. Each of the two pyramids contains three structurally different oxygens, but in total, due to the linking via one common oxygen, there exist five different oxygens and two different vanadiums in γ - V_2O_5 (Table 1).

Bond length (Å)	Vanadyl-Oxygen	Bridge-Oxygen	Chain-Oxygen
$\gamma\text{-V}_2\text{O}_5 - V1$	1.5468	1.7257	1.8914, 1.9861
$\gamma\text{-V}_2\text{O}_5 - V2$	1.5810	1.8479	1.8984, 1.9671
$\alpha\text{-V}_2\text{O}_5$	1.5759	1.7783	1.8776, 2.0176

Table 1: Different bond lengths for the two VO_5 pyramids of the $\gamma\text{-V}_2\text{O}_5$ structure and for the VO_5 pyramid of V_2O_5

FT-IR spectra from the nanorod and nanowire sample, the Na(AOT) and from $\alpha\text{-V}_2\text{O}_5$ purchased from Fluka are displayed in Fig. 3 [10]. The spectrum of the bulk divanadium pentoxide is characterized by three absorption bands centered at 1022, 817 and 580 cm^{-1} . The first band at 1022 cm^{-1} is assigned to the V=O stretching (vanadyl oxygen), the last two at 817 and 580 cm^{-1} are due to V-O-V deformation modes [11].

The spectrum of the Na(AOT) is characterized by several absorption bands between 1750 and 1000 cm^{-1} . These bands are also present in the spectrum of the nanocrystals. The band situated around 1630 cm^{-1} is common to all spectra, and is attributed to molecular water. After subtraction of the Na(AOT) contribution from the nanorods and nanowire spectra, bands are left at 1000, 963, 745 and 537 cm^{-1} for both samples. These bands are shifted towards smaller wavenumbers compared to those of the $\alpha\text{-V}_2\text{O}_5$, and the first band is splitted into two equal components². The splitting and the shift of the 1022 cm^{-1} band of the $\alpha\text{-V}_2\text{O}_5$ into 2 absorption peaks is a consequence of the two inequivalent V=O groups [7], occurring at $d_{\gamma\text{-V}_2\text{O}_5}^1 = 1.581 \text{ \AA}$, and $d_{\gamma\text{-V}_2\text{O}_5}^2 = 1.547 \text{ \AA}$, respectively (Fig. 3).

EELS is applied to probe the local electronic structure and oxidation state of vanadium in $\gamma\text{-V}_2\text{O}_5$. For comparison EELS on $\alpha\text{-V}_2\text{O}_5$ is also present. Ab initio band structure calculations are performed on both systems for the OK edge simulation. The shape of the vanadium and oxygen edges is strongly related to the oxidation state of the vanadium and to the distortion of the coordination polyhedra [12, 13]. In particular, the vanadium white line ratio reacts very sensitively to the oxidation state [14, 15]. The EEL spectrum of vanadium oxide in the energy range 500-560 eV is featured by the VL edges at 519 (L_{III}) and 526 (L_{II}) eV and by

²This splitting cannot be due to the matrix used to make the pellets because FT-IR spectra of nanorods in cesium and sodium chloride pellets have also been recorded and show the same peak positions as for potassium bromide.

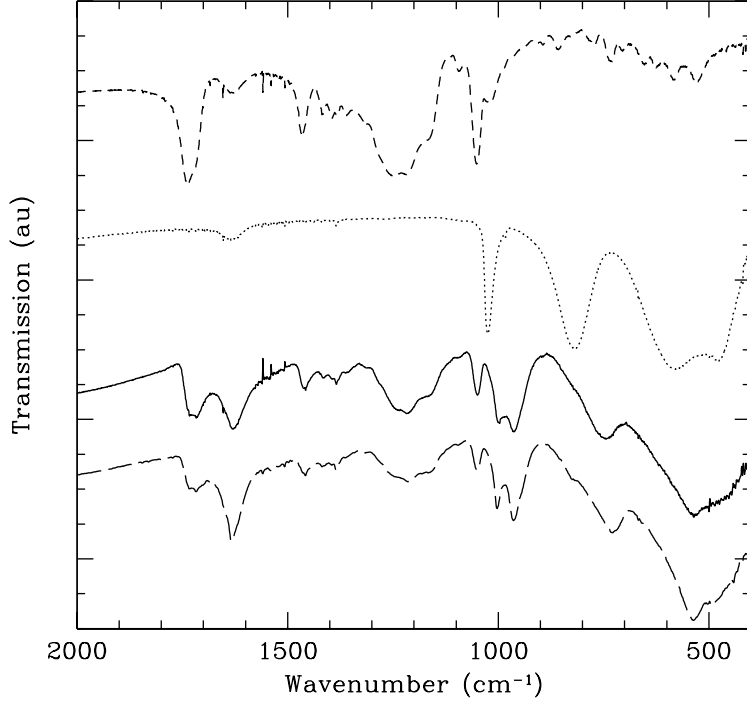


Figure 3: FT-IR spectra of γ - V_2O_5 nanorods (solid line), γ - V_2O_5 nanowires (long dashed line), α - V_2O_5 (dotted line), and Na(AOT) (short dashed line)

the OK edge up from 528 eV. In α - V_2O_5 , the L_{II} edge is more intense than the L_{III} edge [13] (Figure 4 bottom), whereas, with decreasing oxidation state, the L_{II} intensity decreases relative to the L_{III} spectral weight. This fingerprint allows a reliable assignment of the oxidation state of the vanadium. In α - V_2O_5 , the K edge is characterized by a fine structure (Figure 4 bottom) [16]. The oxygen edge around 530 eV exhibits two contributions arising from transitions from an $1s$ state to a final $2p$ state in π^* (530 eV) or σ^* (533 eV) hybridisation with a vanadium $3d$ state. As the oxidation state decreases, the intensity of the first peak related to π^* final states decreases due to a partial filling of the V-d states [17].

The bottom of Fig. 4 demonstrates the close agreement between simulation and experiment, although the core hole left by the excited electron and the high energy tail of the preceding L_{II} edge were not taken into account in the simulation.

EELS spectra of γ - V_2O_5 nanorods and nanowires have been recorded [18] and compared with ab initio calculations [19] (Figure 4). The vanadium L-edge is characterized by two peaks (the white lines) corresponding to the L_{III} transition centered at 518.8 eV and the L_{II} centered at

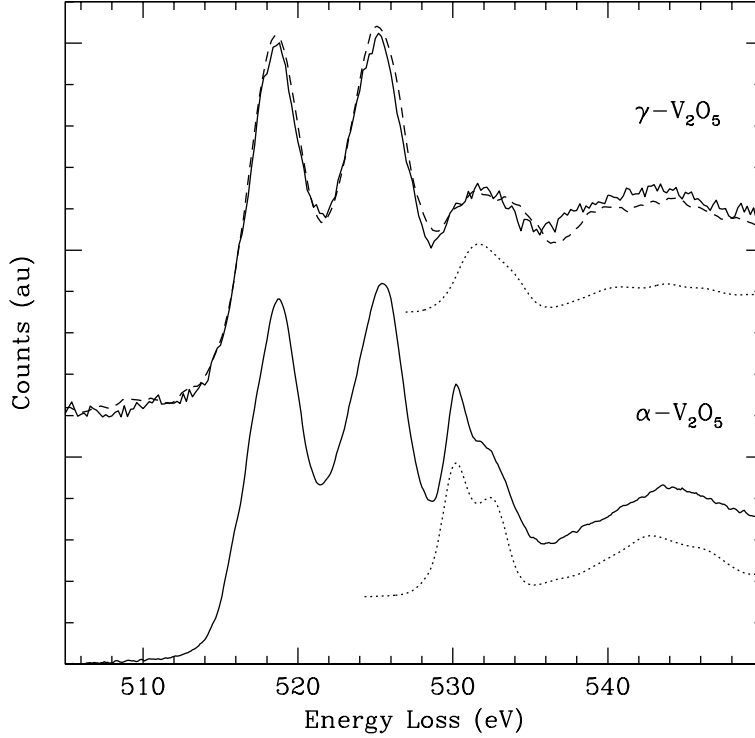


Figure 4: EELS spectra of $\gamma\text{-V}_2\text{O}_5$ nanorods (solid line), $\gamma\text{-V}_2\text{O}_5$ nanowires (dashed line) and for $\alpha\text{-V}_2\text{O}_5$ (bottom) for the Vanadium 2p and the oxygen 1s. Calculations of the oxygen edge (dotted lines)

525 eV. Similar to $\alpha\text{-V}_2\text{O}_5$, the L_{II} peak is more intense than the L_{III} in the spectra of the nanocrystals, indicating that the oxidation state of vanadium is 5+ according to divanadium pentoxide [13]. The shape of K feature centered at 531.6 eV is quite different to the one of $\alpha\text{-V}_2\text{O}_5$. The calculations for the $\gamma\text{-V}_2\text{O}_5$ structure (dotted line in Figure 4), agree very well with the experimental data and show that the fine structure visible in K edge of $\alpha\text{-V}_2\text{O}_5$ is no more present. This is explained by the fact that there exist two different vanadium surroundings in $\gamma\text{-V}_2\text{O}_5$. Five differently coordinated oxygen atoms contribute to the spectrum and the total K spectral weight is the sum of these contributions, of which each has its individual shape. As a result the π^* and σ^* components overlap and are no longer distinguishable in the K edge. It must be pointed out that the shape of the K edge looks similar to the one of the vanadium monoxide (VO), but the position of the edge corresponds to that of divanadium pentoxide (V_2O_5) and could not be attributed to vanadium monoxide [13].

EELS and FT-IR findings confirm that the nanorods and nanowires are crystallized in the

γ -V₂O₅ structure. The results of the samples aged of 24 hours and 100 days are similar even if the size of the particles are different.

This letter demonstrates that a combination of experimental and theoretical tools permit to accurately characterize the local structure, the crystalline order and the surface morphology of γ -V₂O₅ nanorods and nanowires. The uniform material synthesized offers the opportunity to study selective oxidation on model system with well defined surface morphology and high crystalline order containing the oxidation state V⁵⁺ which is difficult to obtain with more conventional physical vapour deposition (PVD) methods.

Acknowledgments

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References

- [1] *Handbook of heterogeneous catalysis*, Vol 4, edited by G. Ertl, H. Knözinger and J. Weitkamp (Wiley-VCH, Weinheim, 1997)
- [2] J. Livage, *Chem. Mat.* **1991**, *3*, 578
- [3] G. R. Patzke, F. Krumeich, R. Nesper *Angew. Chem. Int. Ed.* **2002**, *41*, 2446
- [4] F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, R. Nesper, *J. Am. Chem. Soc.* **1999**, *121*, 8324
- [5] H.-J. Muhr, F. Krumeich, U. P. Schönholzer, F. Bieri, M. Niederberger, L. J. Gauckler, R. Nesper, *Adv. Mat.* **2000**, *12*, 231
- [6] M. Niederberger, M.H. Bard, G.D. Stucky, *J. Am. Chem. Soc.* **2002**, *124*, 13642.
- [7] N. Pinna, U. Wild, J. Urban, R. Schlögl, *Adv. Mat.* **2003**, *15*, 329
- [8] One or more drop of the solution of vanadium oxide nanocrystals are deposited on the amorphous carbon film. A Philips CM200 FEG microscope, 200 kV, equipped with a field emission gun was used. The coefficient of spherical aberration was $C_s = 1.35$ mm.

- [9] J. M. Cocciantelli, P. Gravereau, J. P. Doumerc, M. Pouchard, P. Hagenmuller, *J. of Sol. State Chem.* **1991**, *93*, 497
- [10] Infrared spectra were recorded with a Perkin-Elmer 2000 spectrometer. For FT-IR measurements the nanorods were extracted from micellar solution by centrifugation and washed several times by isooctane to remove the residual AOT. The washed nanorod powder was then incorporated in KBr pellets.
- [11] J. Ryczkowsky, *Catalysis Today* **2001**, *68*, 263
- [12] A Philips CM200 FEG transmission electron microscope equipped with a Gatan GIF 200 spectrometer was used to acquire EELS spectra in image coupled mode. The microscope was operated at 200kV. The recorded EELS spectra were corrected for background and multiple scattering [20]
- [13] D. S. Su, M. Wieske, E. Beckmann, A. Blume, G. Mestl, R. Schlögl, *Catalysis Letters* **2001**, *75*, 81
- [14] R. D. Leapman, L. A. Grunes, *Phys. Rev. Lett.* **1980**, *45*, 397
- [15] J. Fink, Th. Müller-Heinzerling, B. Scheerer, W. Speier, F. U. Hillebrecht, J. C. Fuggle, J. Zaanen, G. A. Sawatzky, *Phys. Rev. B* **1985**, *32*, 4899
- [16] The simulation [19] and the measurements correspond to spectra recorded with the incident beam parallel to the crystal c axis with spectrometer acceptance angle $\beta = 9.8$ mrad and beam convergence angle of $\alpha = 1.5$ mrad.
- [17] C. Hébert, M. Willinger, D. S. Su, P. Pongratz, P. Schattschneider, R. Schlögl, *Eur. Phys. J. B* **2002** *28*, 407
- [18] The spectrum were aquired with a large collection angle and for a large number of nanorods to minimize irradiation effects.
- [19] Calculations were performed using the full potential augmented plane waves package WIEN2k [21] and the TELNES program for simulations of ELNES spectra [22]. The core hole left by the excited electron was neglected. For the calculations the number of k-points was 84 for V_2O_5 and 160 for γ - V_2O_5 . (Gmax=14. RKmax=6.85 for γ - V_2O_5), (RKmax=8 for V_2O_5) The generalised gradient approximation (GGA) was used as exchange-correlation potential [23].
- [20] *Electron Energy-Loss Spectroscopy in the Electron Microscopy* edited by R. Egerton (Plenum, New York, 1996)

- [21] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria), 2001. ISBN 3-9501031-1-2
- [22] C. Hébert-Souche, P.-H. Louf, P. Blaha, M. Nelhiebel, J. Luitz, P. Schattschneider, K. Schwarz, B. Jouffrey, *Ultramicroscopy* **2000**, *83*, 9
- [23] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996** *77*, 3865