X-Ray Absorption Spectroscopy on Low-Dimensional Vanadium Oxide Thin Films

The experimental data have been collected in Total Electron Yield mode to avoid the barium emission (Ba is a component of the substrates). The subsequent analysis has been performed using Ifeffit with the orthorhombic V_2O_5 phase lattice as reference. Figures 1÷2 show the XANES spectra (MA-148) of samples templated with different surfactants and treated at different temperatures.

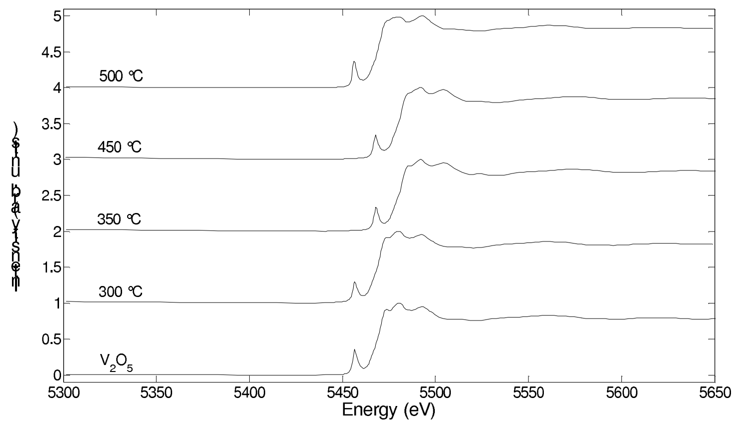

Figure 1 - Examples of XANES spectra of Brij®76 and CTAB templated films. Reference V_2O_5 spectrum has been added.

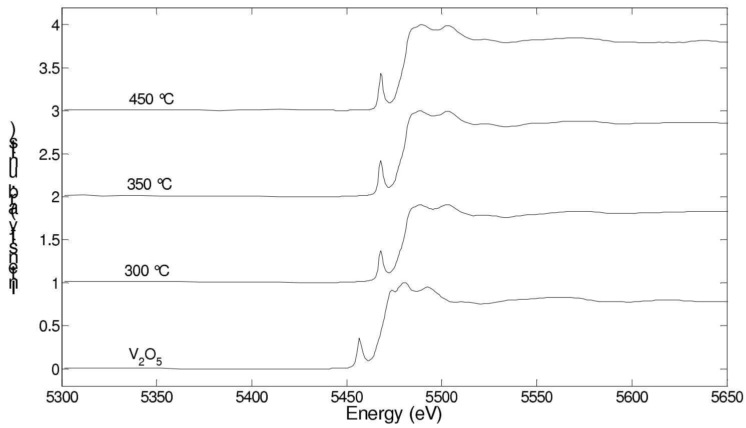

Figure 2 - Examples of XANES spectra of Triton X-100 and Tween-60 templated films. Reference V_2O_5 spectrum has been added.

The rigid shifts of some spectra are due to shifts of the monochromator and to the resetting of the system while performing the XAFS experiments in Grenoble.

All samples show the characteristic pre-edge peak, with intensities comparable to that shown by orthorhombic V_2O_5 phase. Therefore the axial configuration of all the samples must be comparable to that of the orthorhombic phase ($RO_A \approx 1.58$ Å, $RO_{Along} \approx 2.78$ Å).

On the contrary, the near edge features (affected by the symmetry of the equatorial oxygen atoms) seem influenced by the different surfactant used, and show peculiar behaviour.

On one side CTAB and Tween-60-templated films show at intermediate temperatures a broad band that, with increasing temperature, is split into a shoulder and a band, as in the case of the reference V_2O_5 sample. On the contrary, both Brij®76 and Triton X-100-templated materials show at intermediate temperatures the near edge configuration of the reference oxide, while, undergoing thermal treatments, their well-defined near edge structure changes into a more broad and less defined one. It is thus expected that the samples should be characterized by differences in the symmetry of the equatorial oxygen atoms.

EXAFS analysis has confirmed with deeper insights the low temperature crystallization of the orthorhombic V_2O_5 phase giving evidence of some slight differences that can be directly ascribed to the templating agent. In the following discussion all EXAFS experimental $\chi(k)$ have been fitted considering only single scattering shells on an R-range up to 4.2 Å.
Figures 3 show the fits on the k^2-weighted experimental $\chi(k)$ for CTAB-templated samples annealed at 450 °C. The results of the fitting procedures are summarized in Table 1.

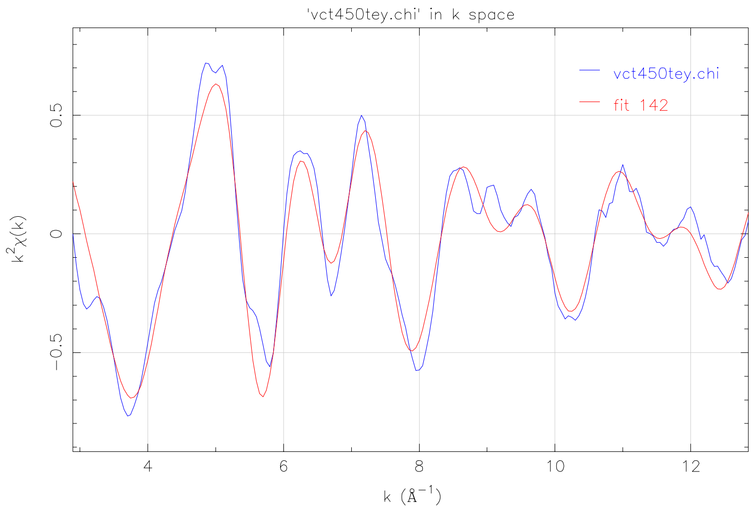

Figure 3 - Fitted k^2-weighted experimental $\chi(k)$ for CTAB-templated samples annealed at 450 °C (k-range: 2.896-12.852 $Å^{-1}$).

Table 1 - Fitting results for the CTAB-templated sample at 450 °C. The amplitude factor has been fixed at 0.9. R_{V2O5} shows the tabulated lengths of the bonds for the orthorhombic V_2O_5 phase.

450 °C	**V-O**					**V-V**	
N	1	1	2	1	1	2	1
R_{V2O5} (Å)	1,586	1,781	1,873	2,022	2,787	3,086	3,425
dR (Å)	0,035	0,045	0,004	0,000	-0,009	0,023	-0,198
σ^2	0,004	0,004	0,001	0,002	0,008	0,004	0,011

It has to be noted that, even at 250 °C, the orthorhombic VO_5 unit is detected and furthermore is characterized by low σ^2 values showing a strong short range order of the constituent VO_5 unit. The order is lost when considering the nearest vanadium neighbour.
As the template is removed upon the thermal treatment, the long range order is increased, and the fit can be extended in R-space at about 4 Å.
Figures 4 show the fits on the k^2-weighted experimental $\chi(k)$ for Triton X-100-templated films annealed at different temperature. The results of the fitting procedures are summarized in Table 2.

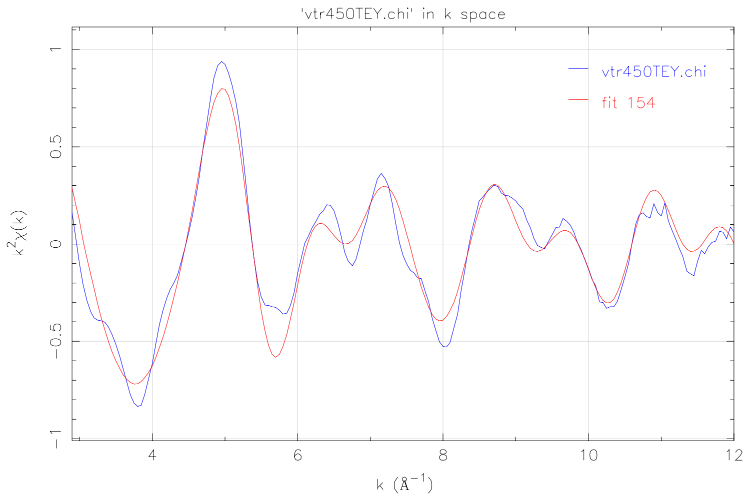

Figure 4 - Fitted k^2-weighted experimental $\chi(k)$ for Triton X-100-templated samples heated at 450 °C (k-range: 2.956-11.690 $Å^{-1}$).

Table 2 - Fitting results for the Triton X-100-templated samples. The amplitude factor has been fixed at 0.9. R_{V2O5} shows the tabulated lengths of the bonds for the V_2O_5 phase.

450 °C	**V-O**					**V-V**	
N	1	1	2	1	1	2	1
R_{V2O5} (Å)	1,586	1,781	1,873	2,022	2,787	3,086	3,425
dR (Å)	0,046	0,030	0,003	-0,029	0,017	0,013	-0,091
σ^2	0,003	0,001	0,003	0,001	0,006	0,005	0,015

Both short and long range order are evident in Triton X-100-templated samples for all the annealing temperatures.
The lengths of the V–O and V–V bonds are comparable with the tabulated orthorhombic values. Just a slight shift of the length of the long $V–O_A$ bond, coupled with a larger σ^2 value, is present in the sample at 300 °C and is consistent with both the removal of the surfactant and with the increasing links between V_2O_4 chains.

For all the annealing temperatures, even for samples heated at 250 °C, the VO_5 unit is detectable showing that the short range order is preserved even when the surfactants are present in the metal oxide network. The presence of ordered VO_5 units is evidenced by the relatively low σ^2 values of the shells of oxygen atoms constituting the first neighbours around the central V_0 atom. Moreover, the possibility to extend the R-region of the fit up to 4.2 Å shows the good crystalline quality of the synthesized nanostructured thin films.
The only slight discrepancies can be detected in the shells of the apical long V–O bond ensuring the cohesion of adjacent vanadium oxide layers and on the nearest vanadium neighbours, located at $R_{V1} \approx 3$ Å. The discrepancies are eliminated by the thermal treatment, that induce further order into the metal oxide framework.
The high temperature samples show EXAFS experimental $\chi(k)$ functions comparable to the commercial orthorhombic V_2O_5 powder. To add more evidences, the forward Fourier Transforms of the k^2-weighted experimental $\chi(k)$ for the samples at 450 °C are shown in Figure 5.

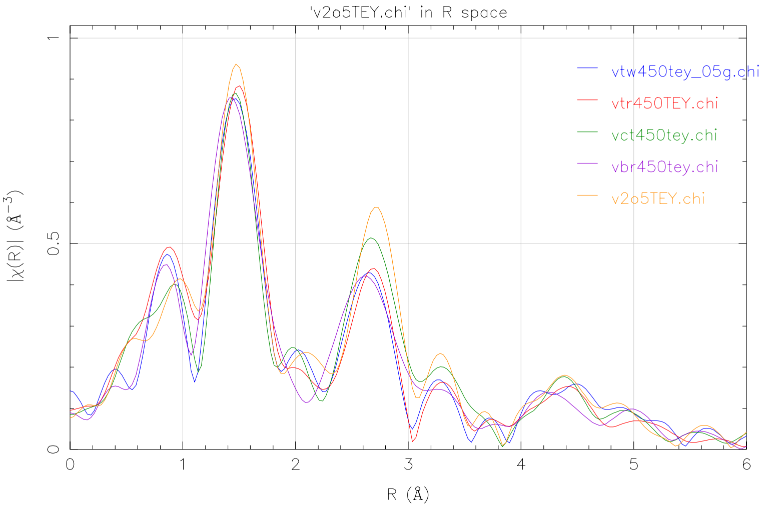

Figure 5 - FFT($k^2\chi(k)$) for films templated with different surfactants and treated at 450 °C. The experimental FFT($k^2\chi(k)$) obtained from commercial orthorhombic V_2O_5 powder has been included as reference.