



Experiment title: Atomic scale structure of Nano-Anatase precursors?

Experiment number:
CH2892

Beamline:
ID26

Date of experiment:
from: 08/04/2009 at 08:00 to 14/04/2009 at 08:00

Date of report:
24/09/09

Shifts:
18

Local contact(s):
Peter Glatzel

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

Rose Jérôme^{2*}, Chanéac Corrine¹, Emmanuel Doelsch^{3*}, Proux Olivier⁴, Hazemann Jean-Louis⁵, Chaurand Perrine^{2*}

1. Laboratoire Chimie de la Matière Condensée de Paris 2 CEREGE UMR CNRS – Aix Marseille Université, Aix en Provence. 3 CIRAD, UR Risque Environnemental lié au Recyclage, SAINT DENIS, Ile de la Réunion 4 Laboratoire de Géophysique Interne et Tectonophysique, UMR CNRS - Université Joseph Fourier, Saint-Martin-D'Hères. 5 Institut Néel, UPR CNRS, Grenoble.

REPORT

Aims of the experiment and scientific background

The project main goal was to investigate the titanium local atomic order within anatase precursors. The nanometric forms of anatase are of a particular interest due to their specifically size-related properties. Therefore the control of size during particle synthesis is a major issue. Anatase can be synthesized by many processes and most often by precipitation from TiCl_4 [1] or TiOSO_4 in aqueous medium. But others processes involved hydrolysis of metallo-organic compounds such as titanium alkoxides in aqueous medium or in microemulsions [2]. Whatever the process an amorphous phase is formed that evolved to anatase upon heating. The crystallisation of anatase is therefore related to the transformation of the amorphous phase. The size, local order and surface properties of the amorphous phase may change from one synthesis process to another. But it clearly appeared that the size, shape and temperature of crystallization of anatase nanoparticles depend on the physico-chemical nature of the amorphous phase. There is no general agreement concerning the parameters governing the phase transformation. In the case of microemulsion the structural characteristics of the amorphous solid precursors and their evolution during thermal treatments have been recently studied [2]. The authors indicated that the precursors showed a local order similar to that of the anatase, but containing undercoordinated Ti_{5C}^{4+} sites. They also indicated that “intraparticle ordering variations determine the temperature for the onset of the nucleation process and drive the solid behavior through the whole crystallization process”. In a recent study the group of the Pr Jolivet (LCMC) ended in an appreciably different conclusion, but for a very different synthesis process[1]. Indeed the synthesis was performed in water without any additive except to control the pH. The amorphous precursors were thought to be more related to Ti-oxyhydroxides structure and then different from the final anatase product. They found that the size of the final product was controlled by the pH of the suspension (the size increased with pH). More exactly “...*The size variation was interpreted as resulting from a lowering of the interfacial tension due to the protonation of particle surface groups...*”. Nevertheless even if precursors with a Ti-oxyhydroxide structure are suspected the modification of the local order of the amorphous precursors as function of size was not totally elucidated.

Experiments

The solids are formed by diluting a stock solution of (TiCl_4) (1 mol/l) and adjusting the pH (from 2 to 6). The final concentration of Ti is 0.1 mol/l. The pH of the mixture is automatically fixed at a selected value and kept constant by addition of NaOH (5 mol/l). For all these samples the precipitation occurs instantaneously and is complete. The amorphous phase is then formed. To form anatase the suspensions are aged in a stove at 60 °C without stirring. The solid is collected after centrifuging the suspension just after the precipitation or after 1, 3, 6, 9, 15, 18, 53 hours of aging. The previous experiment indicated that the crystallisation of anatase is complete whatever the pH after 24 hours [1].

The dried samples were diluted in cellulose and press to form homogeneous pellets. The samples were analyzed in transmission mode.

The emission spectrometer was set up to scan the $K_{\beta 1,3}$ and $K_{\beta \text{ satellites}}$ lines using a Ge331 crystal. RIXS 2D maps were performed prior to scan XANES spectra. The energy resolution of the spectrometer was

Results

RIXS plane surfaces were recorded with incident energy in the 4966-4976 eV energy range and emitted energy in the 4911-4936 eV energy range. From Figure 1, it can be seen that the RIXS surface of the anatase exhibits 3 main peaks at incident energies of 4668,5, 4971,5 and 4873,5 eV (A_1 , A_2 and A_3 peaks) respectively with a strong shoulder at 4970,5 eV (A_2' peak). When scanned at the $K_{\beta 1,3}$ energy, A_1 to A_3 peaks on the XANES clearly appear (figure 2A) but the structure at 4970,5 eV only appears as a shoulder. The evolution of the XANES spectra indicates that the symmetry of the Ti changed from 1h to 4h and then slowly evolved to the anatase structure.

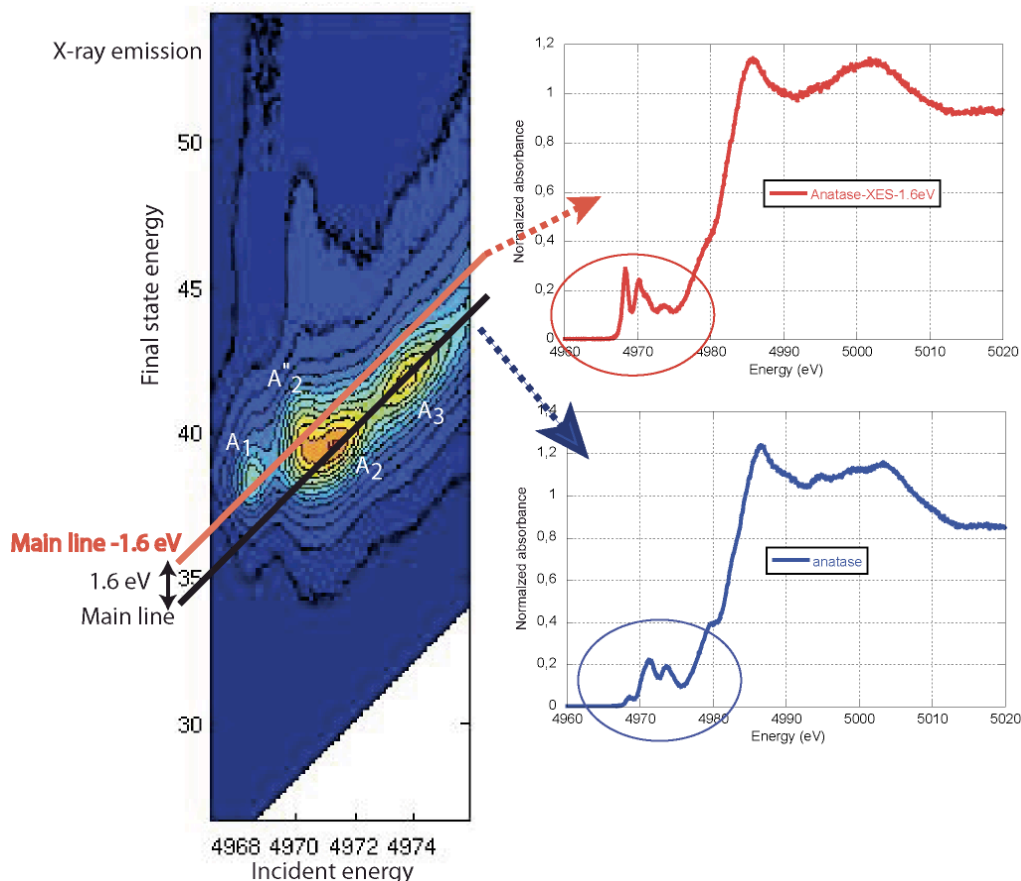


Figure 1: RIXS surface of anatase and XAS spectra recorded with the emission spectrometry at the K_{β} energy and ($K_{\beta} - 1.6$ eV) energy.

By decreasing the energy of the emission spectrometer by 1.6 eV, the pre-edge features of the TiO₂ based nanoparticles are strongly modified. Indeed the A₃ peak almost disappeared while the shoulder at 4970,5 eV, A₂' peak, is modified to an intense peak (Figure 2B).

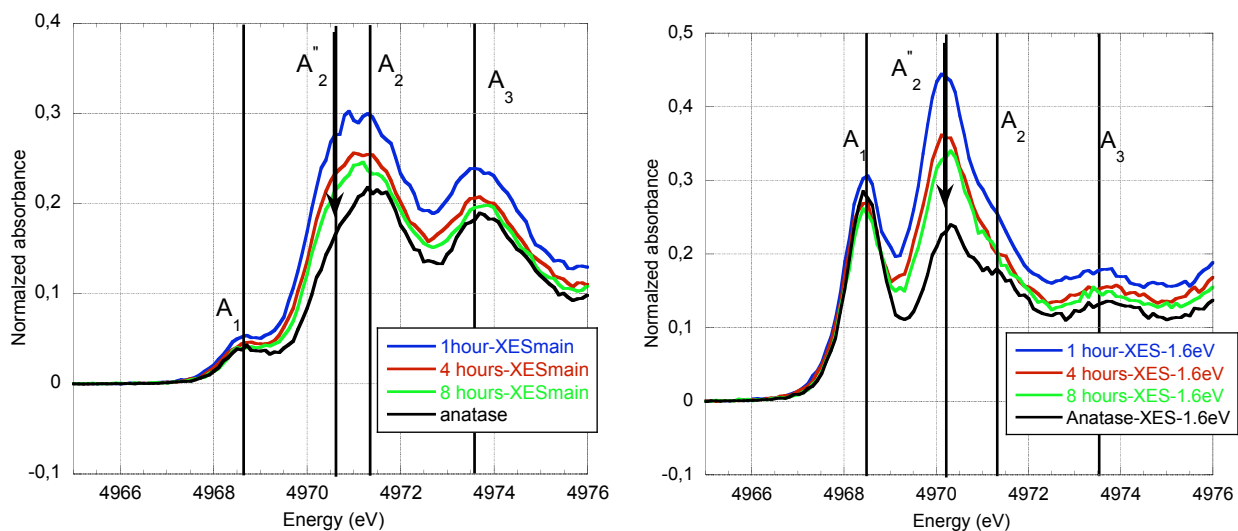


Figure 2: XANES of the samples at various aging time compared to anatase A) recorded at the $K_{\beta 1,3}$ emission energy B) recorded at the ($K_{\beta 1,3} - 1,6$ eV) emission energy.

Based on recent results [3-4] A₁ has been attributed to purely quadrupolar t_{2g} ; A₂ seems to be a dipolar but includes also a minor e_g quadrupolar component while A₃ is a pure dipolar feature. From MS calculations, Wu et al (1997) suggested that A₂ “may be associated with the existence of transition to unoccupied states made up by mixing of Ti-4p orbitals and higher-shell Ti-3d orbitals, and as a consequence they are very sensitive to the ‘medium range’ (5–8 Å) order of the system”. If so the strong decrease of A₂ peak (4970,5 eV) from 1 to 53 hours may indicate a modification of the order. For the 1 h sample the size of the particles is lower than 4 nm, with a high surface/bulk Ti atoms ratio. But also particles are more disordered. For nano system surface relaxation may lead to modifications of the Ti-O bond lengths, resulting in change in the XANES pre-edge features. One of the possibilities can also be a modification from octahedral to penta-coordinated Ti. Unfortunately we did not have pentacoordinated reference samples during the ID26 session to unambiguously conclude.

Since anatase and anatase amorphous precursor exhibit strong structural differences, we have investigated the effects of Ti coordination and symmetry site on the X-ray emission and Raman shift (figure 3A and B respectively).

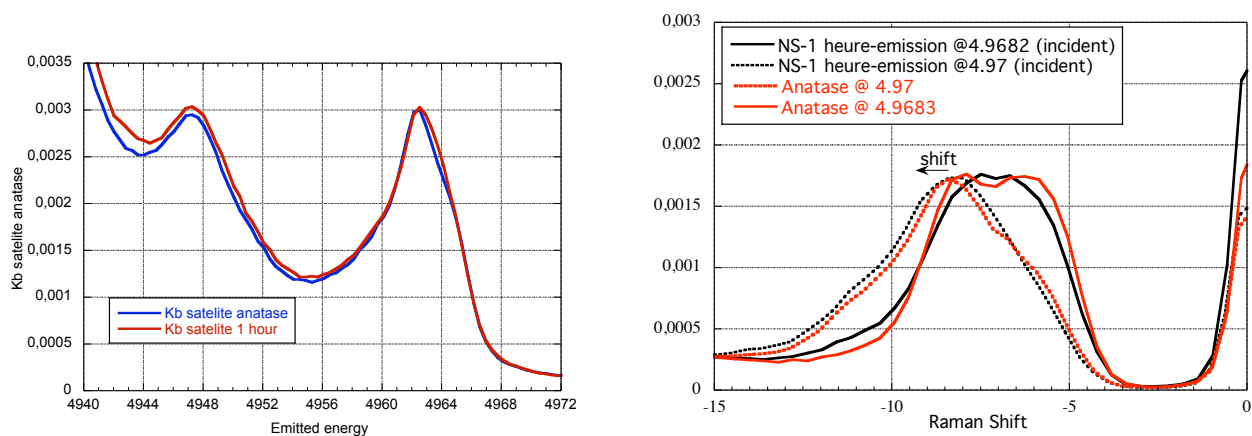


Figure 3: A) K_{β} satellite emission lines for anatase and amorphous anatase precursor B) RIXS for two incident energies (A1 and A2" incident energy respectively).

The 3D atomic arrangement and the size of the particles did not seem to lead to any modifications of the K_{β} satellite emission lines (figure 3A). While it has been shown that the intensity of the emitted peak can be affected by metal ligand distance, in the case of Mn-O [5], in the case of anatase and anatase amorphous precursor, the interatomic structure does not affect the emission.

From figure 3B it is shown that the resonant emission for well crystallized anatase and amorphous precursors exhibits slight different features whether scanned with an incident energy of 4968.2 or 4970.2 eV. In the case of amorphous nanoparticles (after 1 hour) a small shift by -0.2/-0.3 eV seemed to occur. Further investigations are requested to confirm the evolution of the RIXS.

References

- [1] Pottier, A., Cassaignon S., Chanéac C., Villain F., Tronc E., Jolivet J-P., 'Size tailoring of TiO₂ anatase nanoparticles in aqueous medium and synthesis of nanocomposites. Characterization by Raman spectroscopy', *J. Mater. Chem.*, 2003, 13, 877–882.
- [2] Fernandez-Garcia M., Belver C., Hanson J.C., Wang X., Rodriguez J.A., 'Anatase-TiO₂ Nanomaterials: Analysis of Key Parameters Controlling Crystallization' *J. Am. Chem. Soc.* 2007, 129, 13604-13612
- [3] Z. Y. Wu, G. Ouvrard, P. Gressier, and C. R. Natoli, *Phys. Rev. B*, 1997, 55,10382 .
- [4] Y. Joly, D. Cabaret, H. Renevier, and C. R. Natoli, *Phys. Rev. Lett.*, 1999, 82,2398
- [5] U. Bergmann, C.R. Horne, T.J. Collins, J.M. Workman, S.P. Cramer, *Chem. Phys. Lett.* 302 (1999) 119.