ESRF	**Experiment title:** Modification of Ti electronic structure upon molecules adsorption on microporous cristalline titanosilicates: a resonant inelastic X-ray scattering (RIXS) study	**Experiment number**: CH-2988
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Report:

The experiment was successfully performed and, thanks to the high quality of the recorded data, a complete knowledge of the electronic structure of Ti centers in TS-1, ETS-10 and Ti-based Ziegler-Natta precursors was achieved. To summarize, the measurements were performed using the (311) reflections of the Si monochromator for selecting the incident energy and a Ge(331) analyzer crystal. The combined energy resolution (incident and emitted beam) was 1 eV. Measurements were performed at RT and in cryostat (20K) for systems that suffered of radiation damage that was carefully studied for sample. We collected standard and resonant XANES, XES and full RXES maps valence to core (VTC) and 1s3p (core to core or CTC) for TS-1 in (a) vacuum conditions (b) presence of water (liquid and vapor phase) (c) presence of NH_3 (p = 1 atm) (d) presence of H_2O/H_2O_2 solution. Three manuscripts are in preparation to report the acquired data with the respective interpretation based on calculations by means of ORCA (developed by F. Neese and coworker), Feff9.0 (developed by J.Rehr and coworker) and FDMNES (developed by Y. Joly and coworker) code. The

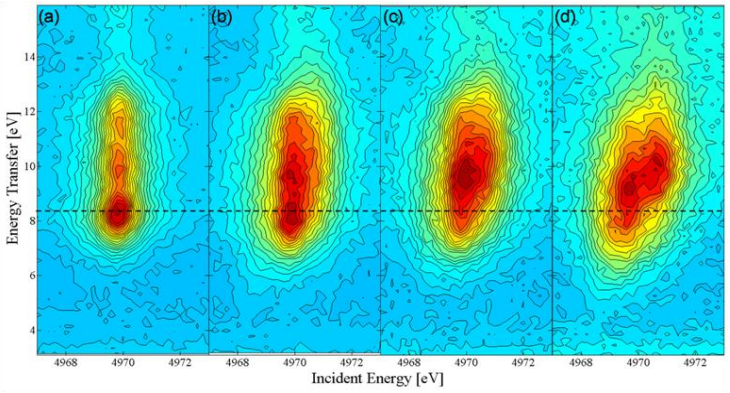

Figure 1. vtc RXES maps for (a) TS-1 degassed (b)in presence of H2O in liquid phase (c)in presence of 1 atm of NH3 (d) in presence of H2O/H2O2 solution

first paper is based on the achieved knowledge on the electronic structure of Ti(IV) centers in TS-1, and the involved molecular orbitals in the Kβ satellites features are discussed by means of a, developed ad hoc, cluster model using ORCA optimization routine. This work was the starting point for the others two where the cluster developed is 1) used to investigate the modification of the valence state of the metal center upon ligand adsorption (NH_3, H_2O and H_2O/H_2O_2) 2) to simulate and understand the valence to core RXES maps and also the pre-edge feature arising in the XANES spectra. Using the RXES maps collected, see Figure 1, we were able to extend the energy region available with UV-Vis measurements and, in this way understand that the UV-Vis spectra show us only the beginning of a complicated structure impossible to reach for standard techniques (see Figure 2 for a comparison) that is linked to ligand to metal charge transfer effect. As it is possible to see from Figure 2 the shift to low energy, that one can see in the UV-Vis spectra (left) between the case of TS-1 degassed and with NH_3 (about 0.4 eV), is an effect of the modification of the main structure between 7 and 13 eV in the RXES maps (*Figure* 1). By means of ORCA we were able to assign for each features the corresponding transition and in this way understand the allowed final states for the system. The transition involved molecular orbital with O character are very interesting because allow us to see that in the case of TS-1 in presence of H2O/H2O2 (measurement performed in cryostat at about 20K) both XANES spectra and RXES map show important changes that we believe linked to the double protonation of H_2O_2 on the metal site as proved by DFT calculation solving the open problem of the interaction of the TS-1 catalyst in its usual environment of work. Furthermore we were able to see, confirming EXAFS data, that in TS-1 the Ti-O(framework) distance changes after ligands coordination: in fact the intensity of the Kβ" satellite line decrease from TS-1 degased ⇨ H_2O ⇨ NH_3 ⇨ H_2O/H_2O_2. As well as for the electronic structure of TS-1, we have investigated the relevant case of Engelhard titanosilicate (ETS-10). The investigated systems were ETS-10 (pure porous titanosilicates – in vacuum conditions), Ag-ETS10 (vacuum condition), H-ETS10 (defective porous titanosilicalite - vacuum condition) and NaN3-ETS10 in order to see the modification of the XANES region using standard XANES measurements and high resolution XANES spectra by whom, using FitIt (A. Soldatov and coworker) we are studying the changes in geometry and electronic structure between pure and defective material in order to solve also the open question regarding the pre-edge region. XES and full RXES maps were collected for all the systems together with the Kβ satellites lines that we have use as in the case of the TS-1. Also in this case the RXES techniques was fundamental because the region of interest is between 7 and 14 eV long the energy transfer axis. In the same region the modification induced in the case of defective ETS-10, Ag-ETS10 and NaN_3-ETS10 lie.

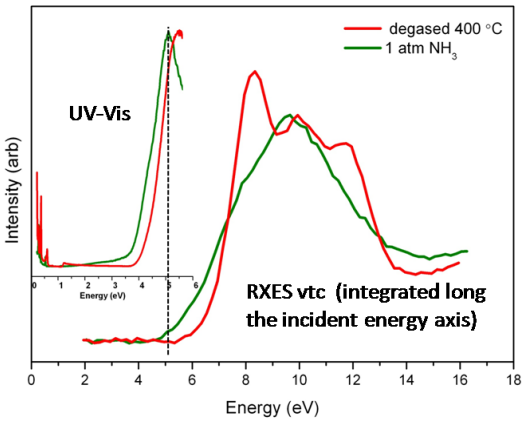

Figure 2. Comparison between UV-Vis spectra (left)and RXES (right - with incident energy integrated).

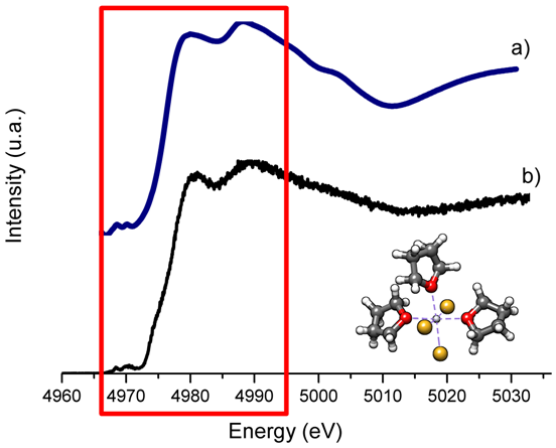

Figure 3. XANES spectra for $Ti(THF)_3Cl_3$. (bottom) Experimental vs (top) calculated spectra by means of FDMNES.

In this series of measurements we were able to collect XANES, Kβ satellites features and a full RXES map for Ti-based Ziegler Natta precursor: $Ti(THF)_3Cl_3$ and $Ti(THF)_2Cl_4$. The results for the valence to core emission spectra of these two important molecular systems are already submitted [1]. The XANES spectra of $Ti(THF)_3Cl_3$ is shown in Figure 3. The XANES region (both pre-edge and edge) was carefully studied and will be very useful for future works on these systems as well as the collected RXES maps that allow us to have information also on the optical region (removing the elastic peak) impossible to achieve with standard fluorimeter (because of solvent problems) for both of them

Acknowledgements

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Publication *[1]* J. C. Swarbrick, Y. Kvashnin, K.Schulte, K. Seenivasan, C. Lamberti, P. Glatzel, *Inorg. Chem.* in press, DOI: 10.1021/ic100755t