ESRF	**Experiment title: XAFS study of Ti-M binary mixed oxides used for photo-catalytic elimination of pollutants**	**Experiment number**: ME-605
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Report:

Photocatalysis is a novel field of great interest for catalytic research with a significant potential to solve environmental problems. The use of anatase-TiO_2 as the base system for photocatalytic processes and the need to further optimize this reference catalyst are well known facts. In particular, its technological application seems limited by several factors among which the most restrictive one is the need of using an ultraviolet (UV) excitation source. The efficient use of solar light or, in other words, of the visible region of the spectrum, may then appear as an appealing challenge for developing the future generation of photocatalytic materials. Recent advances in this field make use of anatase-like Ti-M mixed oxide; the presence of some heteroatoms, like W, into the anatase structure yields the required decrease of the anatase band gap energy and the enhancement of the visible absorption power. The XAFS characterization of these complex oxides is thus necessary in order to interpret their chemico-physical properties.

XAFS experiments were carried at the beam line BM29 with a Si(111) monochromator and the station He cryostat (EXAFS measurements). Series of 5 to 9 Ti-M mixed oxides with growing quantities of the heteroatom were studied for M = W and Zr. Both heteroatoms induce beneficial effects in catalytic elimination of organic pollutants with respect to the bare anatase-TiO_2 reference but Zr makes this only under UV-light excitation while W is able to do it under both UV- and visible-light excitation. Laboratory characterization show that all samples are mixed oxides with anatase-type structure. XANES spectra (Fig. 1) at the Ti-K edge further support the anatase-type crystalline structure of all mixed oxides while EXAFS measurements indicates little differences in the first Ti-O coordination shell with respect to the monocationic TiO_2 reference.

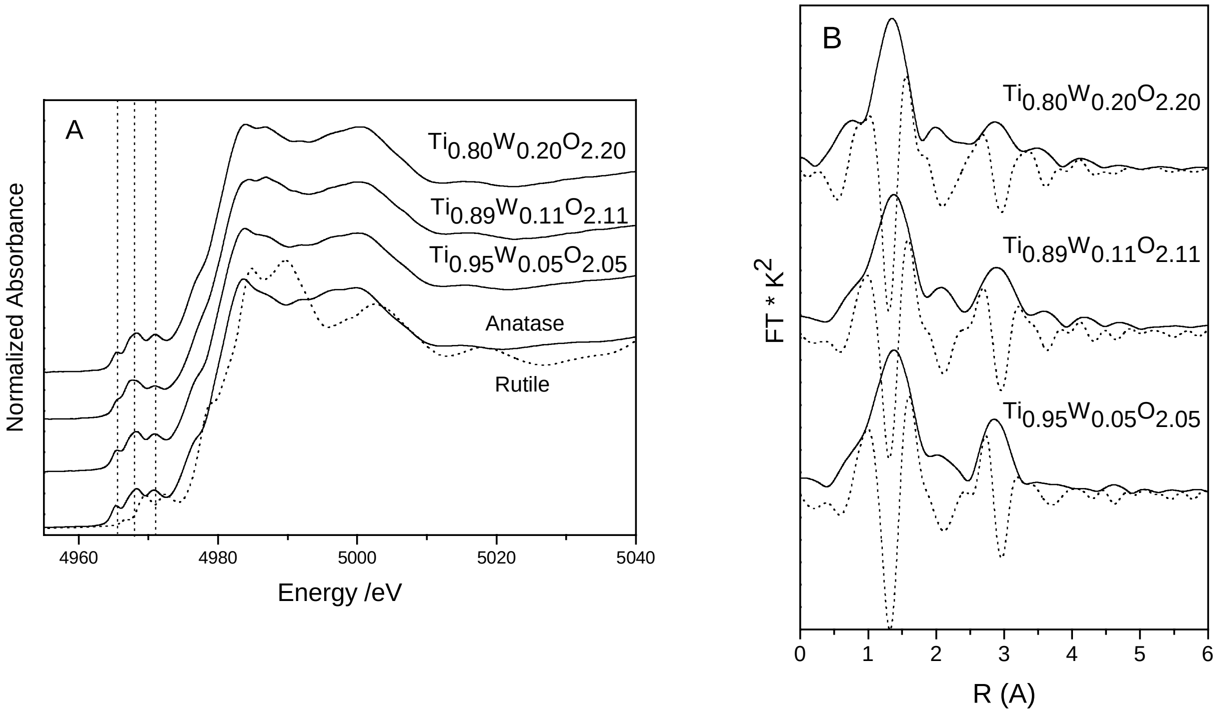

Fig.1. A) Ti K-edge XANES spectra and B) W L_{III}-edge Fourier Transform of EXAFS spectra for Ti-W mixed oxide samples.

In the case of Ti-W mixed oxides, analysis of the W L_I-edge XANES spectra indicates that W occupies low symmetry positions, displaying strong local disorder with respect to cationic positions characteristic of the anatase structure. Analysis of the W L_{III}-edge EXAFS spectra (Fig. 1B) suggests that W has a similar oxygen first coordination and exclusively Ti as second neighbor. Presence of W in the material produces cationic vacancies in order to achieve charge neutrality; as the number of second neighbors around W appears to decrease with W content, this may likely suggest the existence of local order with vacancies preferentially located close to W positions and some W clustering. For Ti-Zr mixed oxides, the XAFS study shows that Zr also occupies low symmetry positions, strongly distorted with those typical of the parent TiO_2 material. Complete analysis of the EXAFS spectra is expected to give adequate input data for theoretical calculations which may interpret the band gap properties of these Ti-based mixed oxide materials.

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