

Report on beam time: CH3407, ID15b

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A multitechnique XAS/XRD/DRIFTS analysis of phase formation and stability in nanostructured, doped TiO₂ and ZnO oxides

Within the 18 shifts allocated to this proposal we were to mount, test and demonstrate the use a new capillary reactor to follow *in-situ* the calcination of oxide precursors using hard using X-ray total scattering and diffraction, complemented with an analysis of evolving gases using mass spectrometry. The capillary reaction was designed in order to minimize temperature and gas gradients during the experiments. The project was originally conceived as a combination of diffraction and absorption techniques but the realization of the absorption part was only (partially) possible afterwards because that part of the project was cut from the current proposal (Director board beamtime limitation of review panels selected Spanish projects). Fortunately, we were able to make a few experiments using an IHR time of Dr. S.F.A. Figueroa at BM23 to complement diffraction experiment.

The initial ID15b run was carried out to analyze doping process of Titania by two elements: Fe as a cationic dopant, well known example related to enhanced chemical activity of the oxide in several chemical reactions (water gas shift, photocatalysis, etc.) and/or S as an anionic dopant, typically present at surface layers, and mostly related to the stabilization of the primary particle size during the calcinations treatment [1]. We analyzed four Fe- (0.5, 1.0, 1.5 and 3 at. %), three S- (5, 10 and 20 at. % at surface), and three Fe/S- co-doped (1.5 at. Fe and the already mentioned S doping quantities) doped samples and the corresponding TiO₂ reference. X-ray total scattering (q range up to ca. 30 Å⁻¹; 2D detector position at 1.3 m from sample) and high resolution diffraction (q up to 7 Å⁻¹; 2D detector position at 0.35 m) experiments were carried out in a single experiment by moving back and forth the detector during a temperature ramp of ca. 3 °C min⁻¹ for RT to 750 °C. All spectra were obtained in ca. 50 s and thus with a temperature uncertainty of ca. 2 °C.

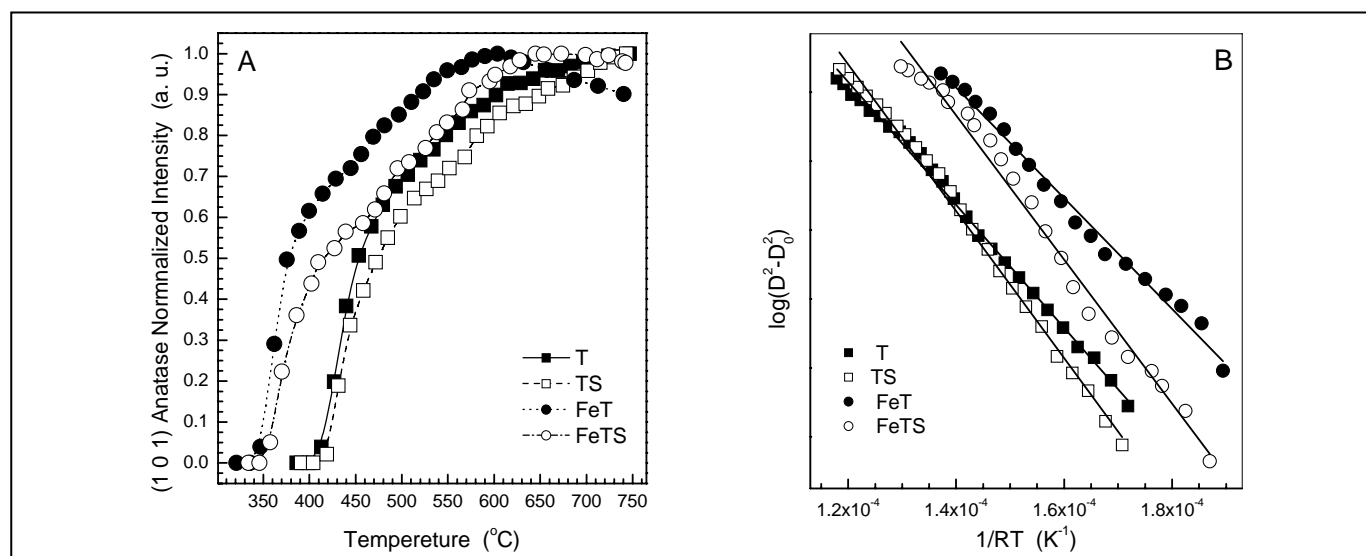


Fig. 1. (A) (101) anatase peak normalized XRD intensity during a calcinations ramp using 1.5 % Fe and/or 20 at. % surface S titania samples; (B) Arrhenius-type plot showing the temperature dependence of the anatase particle size growth as measured by XRD.

XRD data for selected samples are presented in Fig. 1(A). The simple analysis of intensity showed that while Fe strongly modified the nucleation steps of the titania, S does not.

Starting first with the anion, S presence makes exactly the same effect on pure (undoped) and doped Fe samples. This indicates that anion influence on nucleation and growth of oxide primary particle size and thus on particle size control during calcination is/are ground in rather similar physico-chemical bases and are thus of general validity as to field of TiO₂ nanomaterials. The kinetic study of the growth process (Arrhenius-type plot of the process shown in Fig. 1B) provided conclusive evidence of the fact that primary particle size is kinetically controlled by water entities evolution from hydroxyl species of the precursor materials. This particle size growth process showed a consistent (e.g. independent of the Fe presence or absence) increase of the energy of activation by ca. 4 kJ mol⁻¹ in presence of S. A parallel DRIFT study gives evidence that S not only affects the primary particle size but also drives to particle shape elongation along the c-axis with respect to samples without presence of the anion. S thus influences the two more important morphological variables primary particle size and shape and the diffraction-based study was able (in combination with DRIFTS) to understand the physico-chemical bases (a kinetic control linked to water formation during the growth step) of such behaviour. These results were summarized in a manuscript accepted for publication. [2] An additional manuscript focussed in X-ray absorption (XAS) and photocatalytic results was also sent for publication in order to highlight the chemical interest of Fe and/or S (co)-doped TiO₂ samples. [3]

The single case of Fe doping and its particular incidence in the nucleation process of the titania oxide were subjected to a more profound investigation using PDF-XRD (pair distribution function of total scattering data). Fig. 2 gives a detail vision of the extracted PDF-XRD signal for selected samples. While the TiO₂ reference sample displays the (local and long range order of the) anatase structure up to the end of the treatment, the stability of the phase is limited in presence of Fe to ca. 600 °C. More importantly, the PDF evolution with temperature is rather similar for all samples before and around the nucleation onset and only relatively small differences in the middle range (around 4.2 Å) are visible above nucleation as a result of Fe presence.

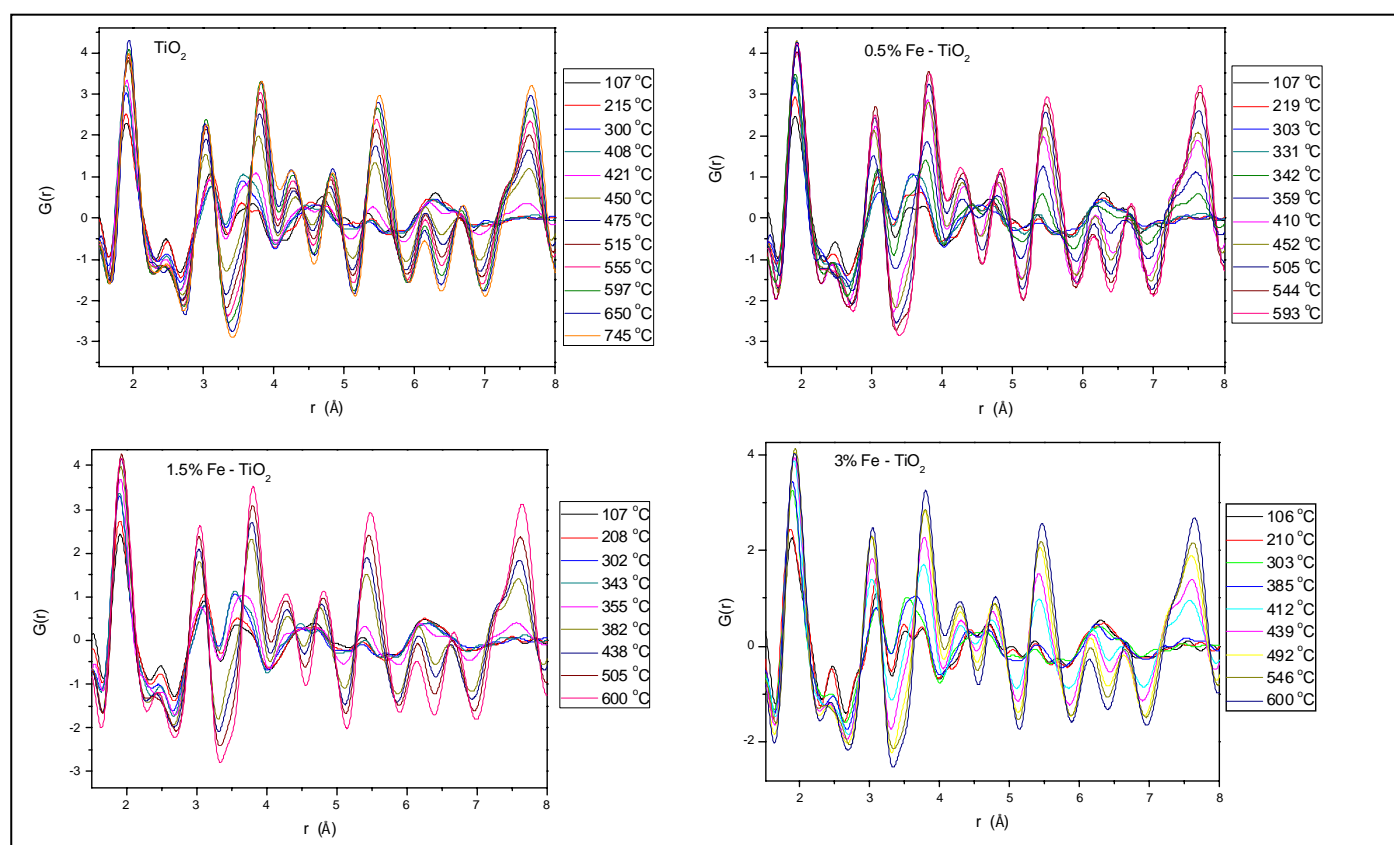
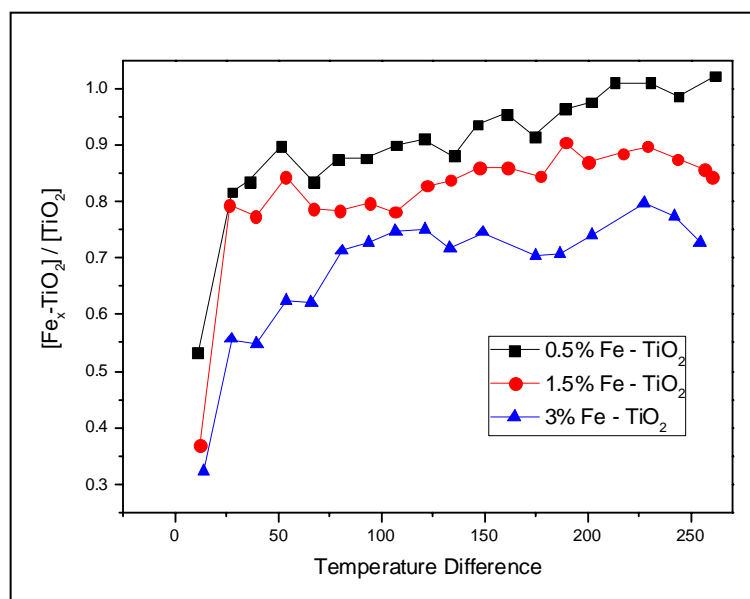


Fig. 2. PDF-XRD data of Fe-doped and undoped TiO₂ materials subjected to a calcinations ramp.

Quantitative analysis of PDF-XRD results is an ongoing project and will elucidate (vide supra) the structural basis of the Fe effect in the nucleation process of the anatase structure of TiO₂ oxide nanomaterials. An initial result comes out from the analysis of the intensity of the peak at ca. 4.2 Å, ascribable exclusively to Fe(Ti)-O distances within the anatase network. Fig. 3 plots the intensity evolution of such peak normalized to one of the undoped material obtained with the same preparation method. The graph describes a progressive influence of Fe as the dopant concentration increases; a disordered-induced effect in turn intimately related to the defect structure to achieve charge neutrality. It appears that the main point defect present in Fe-doped TiO₂ is a cationic vacancy with concomitant presence of OH species. [1] Although such defect species are apparently quasi-randomly distributed in Fe-doped samples, a higher probability of being at the second Cation-Cation coordination distance seems possible in our samples,



generating disordering in the neighbouring Fe-O shell. An alternative possibility is the presence of anion-vacancies mainly driven by the nanometer size of the materials. [1] Full analysis of the PDF signal is rather complex due to the fact that Fe effects are smeared out in a TiO₂ network where a significant number of cation atoms are not affected by the heteroatom. Currently, our attempts to fit the PDF spectra using both Fe-defect models do not allow to obtain an unambiguous answer due to the high number of free parameter derived from the initial information available (even using the information of the local ordering around Ti and Fe –XAS- and specific fitting procedures for amorphous-type materials [4]).

Fig. 3. Normalized PDF peak intensity at 4.2 Å of Fe-doped TiO₂ samples with respect to the undoped material.

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References

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