

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Defects in Fe-doped TiO ₂ photocatalysts for NO _x remediation	Experiment number: 26-01-861
Beamline: BM26A	Date of experiment: from: 27/11/2009 to: 30/11/2009	Date of report: 31/08/2010
Shifts:8	Local contact(s): Dr. S. Nikitenko	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Qingping Wu [*] , Qiang Zheng [*] and Roel van de Krol [*] Delft University of Technology, Faculty of Applied Sciences, Chemical Engineering / Materials for Energy Conversion and Storage Julianalaan 136, 2628 BL Delft, The Netherlands		

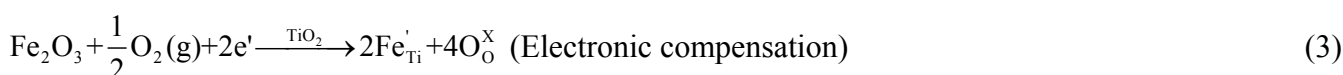
Report:

Introduction

Titanium dioxide (TiO₂), one of best-known semiconductor photocatalysts, is able to decompose NO_x present in air [1]. However, TiO₂ photo-oxidizes NO_x to NO₃⁻ ions, which do not spontaneously desorb and therefore de-activate the TiO₂ surface. Previous work on Ti-impregnated zeolites has shown that a reduction of the Ti coordination number of TiO₂ from 6 to 4 changes the reaction mechanism from the photo-oxidation of NO to photo-reduction into N₂ and O₂, thereby elegantly avoiding the de-activation of the photocatalyst [2]. Our aim is to reduce the coordination number of Ti in TiO₂ nanoparticulate photocatalysts by creating a large number of oxygen vacancies. This can be done by annealing the sample in vacuum (Eq. (1)), but since this reaction is reversible the oxygen vacancies will slowly disappear under ambient conditions.



We aim to stabilize these vacancies by doping the TiO₂ with Fe ions. The incorporation reaction is irreversible, and can be written in two ways, depending on the p(O₂) and the background concentration of electrons:



The aim of this XANES/EXAFS study is to i) prove that Fe doping introduces oxygen vacancies and tetrahedrally coordinated Ti, ii) investigate the valence state of the Ti ions (4+ or 3+), and iii) determine the distribution of Fe dopants and the tetrahedrally coordinated Ti ions within the TiO₂ nanoparticles.

Experiments

The X-ray Absorption Fine Structure (XAFS) experiments were performed on the DUBBLE beamline (BM26A) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), operating under beam condition of 6 GeV, with beam currents ranging from 160 mA to 200 mA. All Fe doped TiO₂ (Fe/TiO₂) samples are prepared by sol-gel method and the crystal sizes are well controlled approximately 10 nm. About 5 mg of the samples mixed with 50 mg BN (99.5%) were pressed into a pellet. Measurements took place at room temperature in air in transmission mode for Ti K-edge (4966 eV) and fluorescence mode for Fe K-edge (7112 eV). The beamline is equipped with a Si (111) double-crystal monochromator, which is detuned to

60% of the bragg peak intensity to suppress higher harmonic. For the fluorescence mode, a 9-element Ge solid state detector is used.

The EXAFS data are extracted from the measured absorption spectra with XDAP software [3]. Three scans for each sample are averaged together to improve the signal-to-noise ratio. The edge-energy is determined from the maximum of the first derivative of the spectrum and calibrated with the reference Ti or Fe foil. A smooth atomic background function, represented by a cubic spline, is used to extract the EXAFS oscillation from the absorption spectrum. The obtained data are normalized by the background height 50 eV after the edge. Experimental data are fitted in R-space, using the difference file technique in real space. The quality of the fit is checked by applying k^1 and k^3 weightings.

Results and discussion

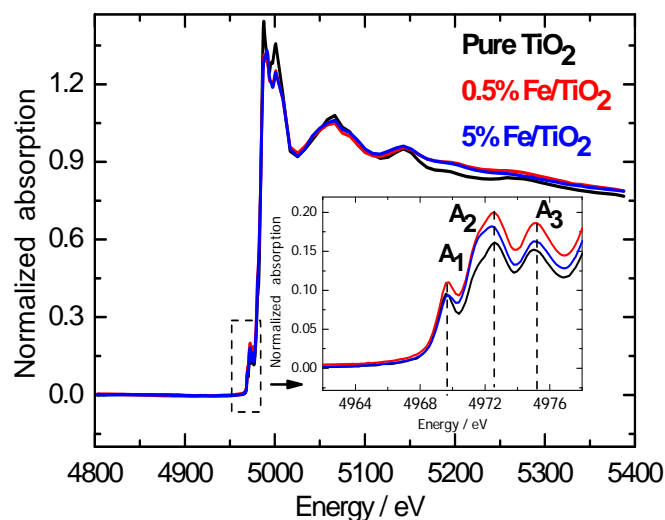


Fig. 1 Ti K-edge XANES for Fe/TiO₂ after annealing at 723 K and pure TiO₂ reference.

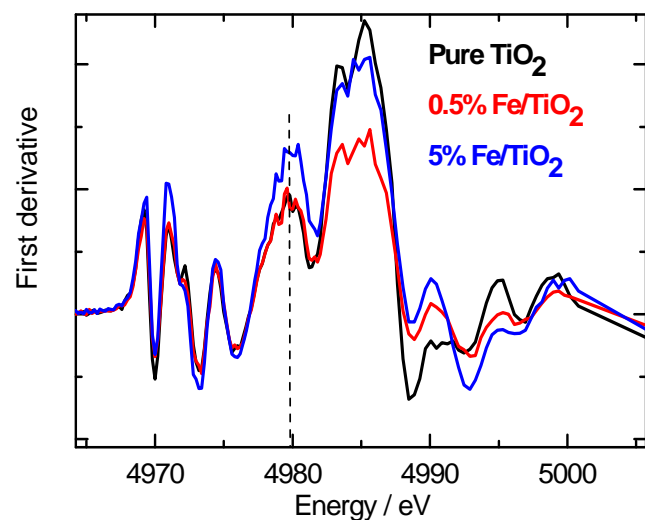


Fig. 2 First derivative of Ti K-edge XANES for Fe/TiO₂ after annealing at 723 K and pure TiO₂ reference.

Ti K-edge XANES spectra are used for identifying the electronic structure and valence state of the samples. XANES spectra of commercial pure anatase, 0.5% Fe/TiO₂ and 5% Fe/TiO₂ are shown in Fig. 1. The three low intensity pre-edge peaks (A₁, A₂, A₃) for all samples are attributed to the transition from 1s core level of Ti to three different kinds of molecular orbitals ($1t_{1g}$, $2t_{2g}$ and $3e_g$) and are related with the octahedral coordination of Ti in TiO₂ lattice [4,5]. The presence of tetrahedrally coordinated Ti would result in a single peak between the A₁ and A₂ peaks [6]. Comparing with pure TiO₂, a small increase of the shoulder peak intensity at ~4971 eV for 5% Fe/TiO₂ (and to a smaller degree also for 0.5% Fe/TiO₂) is indeed observed, indicates that a small amount of tetrahedrally coordinated Ti is formed upon high Fe doping.

The onset of the Ti K-edge XANES spectra is defined by the first maximum of the first derivative for the main edge-jump. No shift of this peak is observed upon Fe doping (Fig. 2), indicating that the titanium ions remain in the 4+ valence state. This is indeed consistent with the ionic compensation mechanism of Eq. (2), which shows that Fe can be incorporated into the TiO₂ lattice without creating or consuming any free electrons.

The Fourier transformed Ti K-edge EXAFS data of pure TiO₂ and Fe/TiO₂ are plotted in Fig. 3 without phase correction. Compared with pure TiO₂, the Ti-O bond length has actually shrunk by about 0.15 Å for 5% Fe/TiO₂, while Ti-O bond length remains almost the same for 0.5% Fe/TiO₂. This is contrary to what is expected, since the radius of Fe³⁺ ions (0.65 Å) is bigger than that of Ti⁴⁺ (0.61 Å) for six-fold coordinated ions [8] and the big Fe³⁺ ions are expected to expand Ti-O lattice.

We explain the observed lattice decrease by a large amount of oxygen vacancies that are created to charge-compensate the high concentration of Fe dopants (5%) according to Eq. (2). The attraction between the

negatively charged Fe_{Ti}' and positively charged $\text{V}_{\text{O}}^{\bullet\bullet}$ may result in the formation of $(\text{V}_{\text{O}}^{\bullet\bullet} - 2\text{Fe}_{\text{Ti}}')^x$ defect associates, especially at high Fe concentrations (5%). The combined effect of a vacancy and a slightly larger substituent explains the observed reduction of the interplanar spacing of TiO_2 .

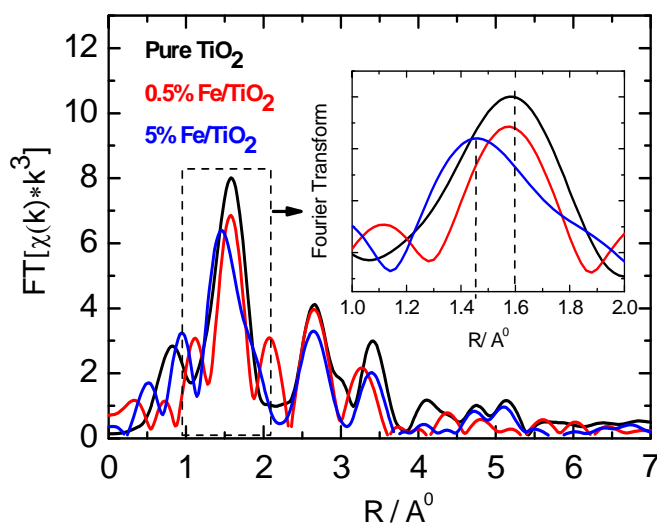


Fig. 3 Magnitude part of phase-uncorrected Fourier transformed k^3 -weighted $\chi(k)$ of Ti K-edge EXAFS spectra for pure TiO_2 and Fe/TiO_2 .

An alternative explanation for the ~ 0.15 Å shrinkage of Ti-O bond for 5% Fe doped TiO_2 is the formation of tetrahedral Ti. This has indeed been observed for (amorphous) Ti/Si mixed oxides, in which a Ti:Si ratio of 1:8 resulted in a Ti-O lattice distance of 1.82 Å, compared to 1.94 Å for pure anatase TiO_2 [9]. However, under these conditions Liu et al. [9] also observed a large pre-edge peak at ~ 4970 eV, confirming the presence of tetrahedrally coordinated Ti. Since only a minor shoulder at this energy is observed in Fig. 1, we conclude that the 0.15 Å decrease in Ti-O distance is primarily due to the large concentration of oxygen vacancies in our Fe/TiO_2 system.

In summary, our main research questions have already been answered by the preliminary analysis: at relatively high concentrations (5%), Fe doping indeed results in the formation of a large amount of oxygen vacancies and a concomitant decrease of the Ti-O bond length. The latter result is consistent with X-ray diffraction analysis results (not shown here). Furthermore, a small pre-edge XANES shoulder at ~ 4971 eV suggests that a small amount of tetrahedrally coordinated Ti is also present in our system. Detailed analysis of the Fourier transformed EXAFS data for the Ti and fluorescence Fe K-edges is still in progress and is expected to give exact number of Ti coordination, correct Ti-O bond length and reveal the distribution of the Fe ions on TiO_2 nanoparticles.

References

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