



## 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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can 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.



	<b>Experiment title:</b> Changes of Ti coordination in titanium phosphates and their consequences on N <sub>2</sub> and H <sub>2</sub> adsorption at elevated temperatures	<b>Experiment number:</b> 25-01-1028
<b>Beamline:</b>	<b>Date of experiment:</b> from: 19.05.2017 to: 23.05.2017	<b>Date of report:</b>  <i>Received at ESRF:</i>
<b>Shifts:</b>	<b>Local contact(s):</b> Eduardo Salas-Colera	
<b>Names and affiliations of applicants (* indicates experimentalists):</b> Igor Krivtsov Marina Ilkaeva Jorge García-González  Department of Organic and Inorganic Chemistry, University of Oviedo, 33006 Oviedo, Spain		

## Report:

The present research aimed to evaluate the role of titanium local arrangement in the dehydrated titanium phosphates on the adsorption of hydrogen and nitrogen gases under elevated temperatures. The in-situ XAS study of the adsorption process will help to establish the adsorption mechanism by tracking the changes in oxidation state of titanium atoms, its coordination number and the bond distances in the first and the second coordination spheres. The knowledge obtained through the proposed experiment will contribute to the elaboration of the titanium phosphate based heterogeneous catalysts for the ammonia production.

X-ray absorption data were collected around Ti K-edge using a -70 °C ethanol cooled double Si(111) crystal, which gave an energy resolution of  $\Delta E/E = 1.5 \times 10^{-4}$ . The experiment was performed at room temperature in fluorescence mode at standard 45° geometry. For fluorescence detection, Sirius liquid nitrogen cooled multi-element solid state X-Ray detector from e2v was employed. The detector included 13 Si(Li) crystal sensors mounted on a low noise electrically restored FETs. The samples were measured in the energy range from 4.8 to 5.7 keV.

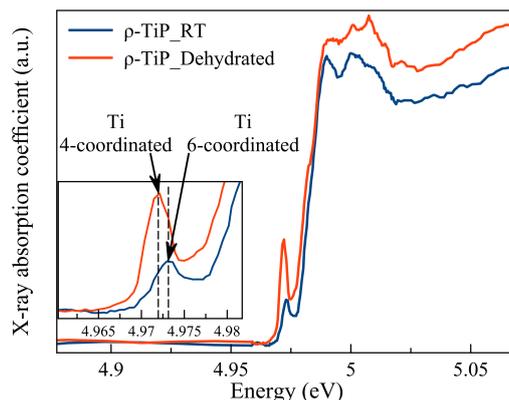


Figure 1. XANES data and the XANES pre-edge region of dehydrated titanium phosphate.

The XANES study has proved the earlier proposed hypothesis (J. García-Glez, Z. Amghouz, I. da Silva, C. Ania, J.B. Parra, C. Trobajo, S. García-Granda, Chem. Comm. 2017, **53**, 2249) about the change of titanium coordination from 6 to 4 in dehydrate titanium phosphates ( $\rho$ -TiP). From Figure 1 it is clearly seen that the pre-edge peak characteristic of titanium coordination is displaced after the material being dehydrated. We consider that the changes of titanium coordination after dehydration and formation of tetraordinated Ti-species is determinative for its ability to adsorb  $N_2$  at high temperatures. The in-situ XANES and EXAFS study of the  $N_2$  adsorption-desorption cycles on the titanium phosphate has also been carried out and the data obtained are being evaluated.