



# EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

## 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> HERFD-XANES and XES studies of V-W-TiO <sub>2</sub> catalysts for NO <sub>x</sub> removal by selective catalytic reduction	<b>Experiment number:</b> CH-4419
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 22.04.2015 to: 28.04.2015	<b>Date of report:</b>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Lucia Amidani	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Dr. Federico Benzi <sup>*,1</sup> Dr. Maria Casapu <sup>*,1</sup> Dr. Dmitry Doronkin <sup>*,1</sup> Tobias Günther <sup>*,1</sup> Enrico Japke <sup>*,1</sup> Prof. Dr. Jan-Dierk Grunwaldt <sup>1</sup> <sup>1</sup> <b>Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Engesserstr. 20, 76131 Karlsruhe</b>		

## Report:

V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> catalysts are widely used to selectively reduce the NO<sub>x</sub> in the exhaust gas of various stationary sources but also mobile applications such as *e.g.* trucks and ships. Conventional XAS cannot be directly applied for studying the V sites in the case of V-W-TiO<sub>2</sub>, since W is highly absorbing around V K edge compromising transmission measurement and Ti fluorescence lines almost overlap with those on V when using standard fluorescence detection techniques. To overcome these challenges we performed a series of HERFD-XANES and V2C XES measurements at the ESRF ID26 beamline.

The catalyst used in this study consisted of 2wt.% V – 9wt.% W on TiO<sub>2</sub> with a surface area of 70 m<sup>2</sup>/g. The catalyst was pressed, crushed and sieved to obtain a fraction of 0.13 – 0.25 mm. The catalyst powder was placed inside a 1 mm quartz capillary serving as a micro reactor. It was mounted on top of a hot air gas blower (Oxford GSB-1300) connected to the gas dosing system. Gases were provided from gas bottles and dosed by mass flow controllers (Bronkhorst). Water vapor (3% H<sub>2</sub>O) was dosed via a saturator. The catalyst was heated from room temperature to 550 °C in He for cleaning purposes and the temperature and gas flow was kept constant for the whole experiment. Twenty different gas compositions have been analysed during the beamtime, alongside a set of model compounds representative of the most common V coordination geometries and oxidation states.

To study the reaction mechanism for the selective catalytic reduction over vanadium it was necessary to analyse different compositions of gas mixtures to identify different features in the spectrum evolving from different chemical reactions.

By comparing the pre-edge peak centroid position and intensity of model compounds (with pure speciation) with that of the sample under different gas feeds we see a clear change of V speciation as a function of the gas atmosphere.

The presence of  $\text{NH}_3$  or  $\text{C}_3\text{H}_6$  without any other reactants reduces the vanadium with respect to the *ex situ* results from the pellets. Its speciation is comparable to a pure octahedral  $\text{V}^{4+}$ . On the other hand the presence of  $\text{NO}$  or  $\text{O}_2$  without any other reactant partly oxidises  $\text{V}$  up to an intermediate state between +4 and +5 (Figure 1). Due to the competition of reactants on the active sites of the catalyst some of these changes cancel out each other if more reactants are present. For an example the capability of  $\text{C}_3\text{H}_6$  to reduce the catalyst is not detectable if the gases for a standard SCR composition are present.

We could see a difference in the signal for a standard SCR gas composition if the temperature changes. Increasing the temperature from  $250\text{ }^\circ\text{C}$  to  $400\text{ }^\circ\text{C}$  leads to a shift of the pre-edge feature to higher energies. Due to the possibility to perform spatially resolved measurement we could also see that there is a difference as well. If there is no water present the oxidation state of the catalyst will raise from inlet to outlet in a standard SCR feed with  $\text{V}$  having the highest oxidation state at the outlet (Figure 2).

From this experiment, HERFD-XANES has proved to be one of the few tools which allows to gather insights into the  $\text{V}$  speciation in a sample of great technological impact which has a critical composition such as  $\text{V-W-TiO}_2$  catalysts. We have been able to differentiate the  $\text{V}$  oxidation state and local geometry under a number of different model and realistic reaction conditions. The combination of our *in situ* setup, which allows to simulate realistic conditions, and the modern photon in – photon out spectroscopic techniques available at ID26 open a new set of possibilities to study catalytic systems previously experimentally inaccessible.

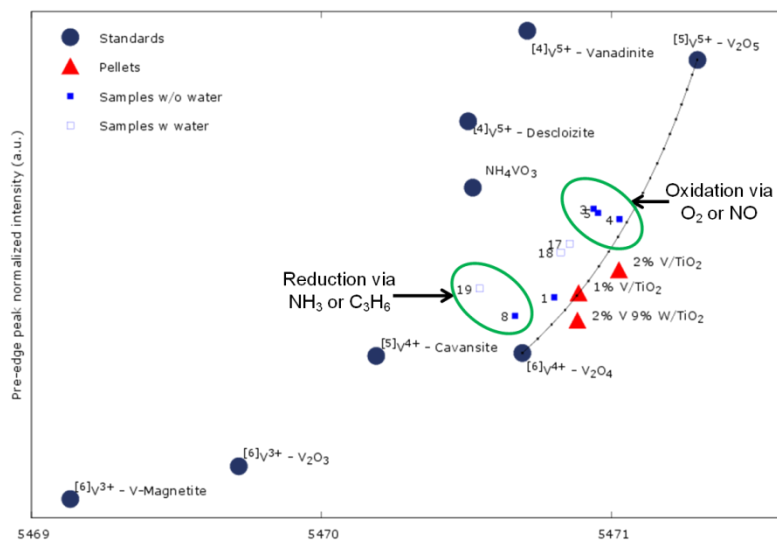


Figure 1: Normalized intensity versus the centroid position of the pre-edge peak. Shown are the results from standards and the resulting reduction/oxidation from gas mixtures containing  $\text{NH}_3$ ,  $\text{C}_3\text{H}_6$ ,  $\text{O}_2$  or  $\text{NO}$ .

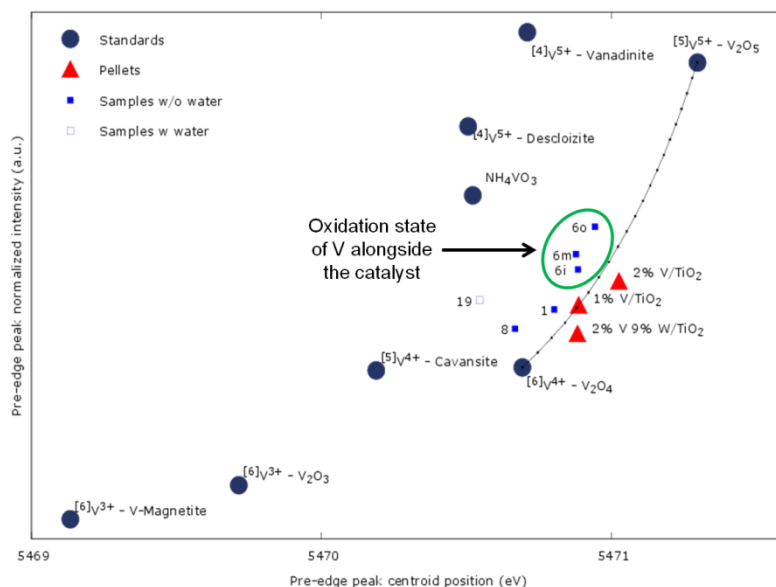


Figure 2: Normalized intensity versus the centroid position of the pre-edge peak. Shown is the change of the oxidation state of  $\text{V}$  alongside the catalyst in a SCR composition without  $\text{H}_2\text{O}$ . (6i: inlet / 6m: middle / 6o: outlet)