



	Experiment title: Hydrogen production over iron oxide catalysts: in situ XAS investigation of the iron oxide reduction/oxidation behaviour	<b>Experiment number:</b> 26-01-910
Beamline: BM26A	Date(s) of experiment : 31/3 – 5/4/2011	<b>Date of report:</b> 15/5/2011
Shifts: 15	<b>Local contact(s):</b> Sergey Nikitenko – Miguel Silveira	
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## Report: (max. 2 pages)

### Introduction

The aim of the experiment was to obtain first structural information about the Fe environment for 3 catalysts, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>/CeZrO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>, during redox treatments by *in-situ* X-ray absorption spectroscopy (XAS) in transmission at the Fe K edge.

### Problems encountered

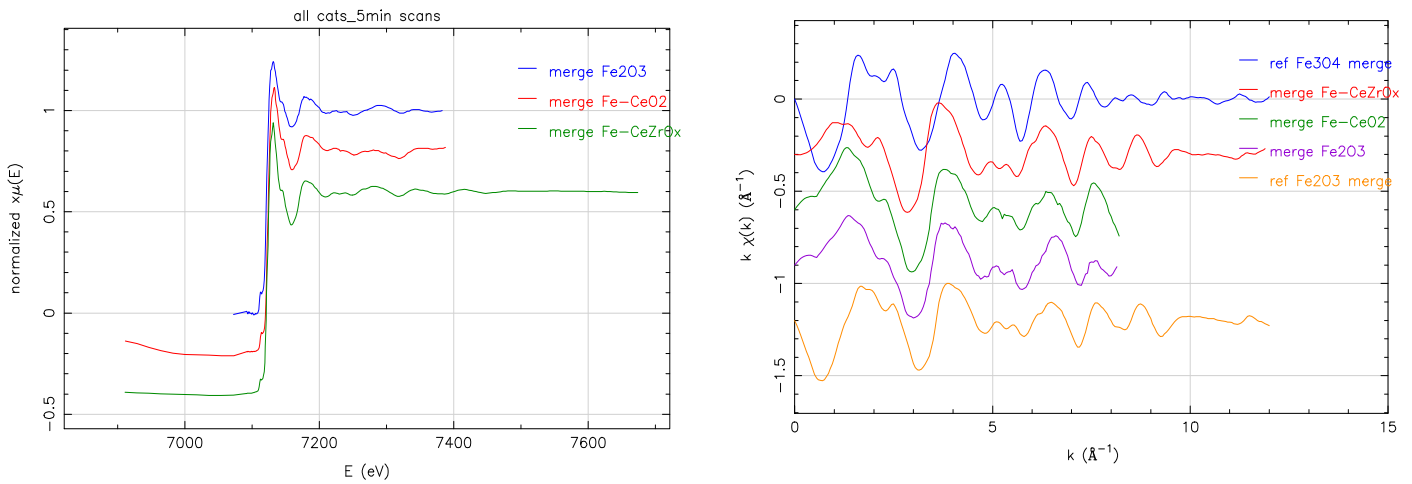
The grain structure of the catalyst powder was such that the sample loaded into a capillary container was not homogeneous enough and gave rise to a distorted signal, due to vertical beam displacement during energy scanning. This was partly overcome by extra grinding of the material and switching to a pellet reactor cell. During the beam time, the monochromator ran into a time-out error a few times. Resetting of the mono inside the optics hutch was required, followed by recalibrating with an Fe foil.

### Experiments performed

On all samples, series of redox experiments were performed. During change of state experiments, 1 minute QEXAFS scans were taken, while in fixed state some 5 minute scans were recorded. Reduction implied mostly hydrogen TPR or isothermal reduction, while reoxidation was performed using both O<sub>2</sub> and CO<sub>2</sub>. Several iron oxides, FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, as well as Fe foil were measured as reference oxidation states.

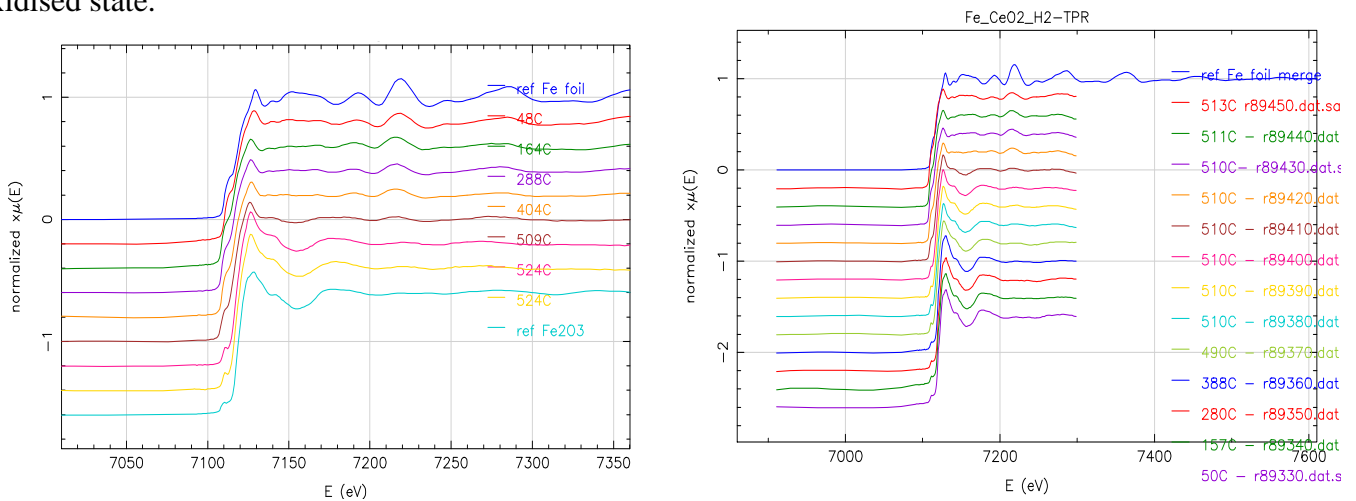
### Results

The 3 catalysts Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>/CeZrO<sub>2</sub> were measured at room temperature in air to compare the Fe oxidation state and environment. From comparison of the normalised absorption (Fig. 1 left), there are little differences between the 3 Fe signals, some of which may be due to lower signal quality. In k-space, the k-weighted EXAFS signals are compared with the ones of powder references Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> (Fig. 1 right). Best correspondence exists with the signal of Fe<sub>2</sub>O<sub>3</sub>, indicating that the Fe is essentially in a 3+ state with ferric oxide structure.



**Figure 1** : left : normalised absorption signal for the 3 catalysts,  $Fe_2O_3$ ,  $Fe_2O_3/CeO_2$  and  $Fe_2O_3/CeZrO_2$ ; right:  $k$ -weighted EXAFS signal for the 3 catalysts and for powder references  $Fe_2O_3$  and  $Fe_3O_4$ .

On all samples, series of reduction and oxidation treatments were performed, either isothermally or temperature programmed. Figure 2 shows the  $H_2$ -TPR and subsequent  $CO_2$ -TPO from room temperature to  $\sim 525^\circ C$  over  $Fe_2O_3/CeO_2$ . Reduction brings down the Fe oxidation state to close to 0, while  $CO_2$  is able to restore an oxidised state.

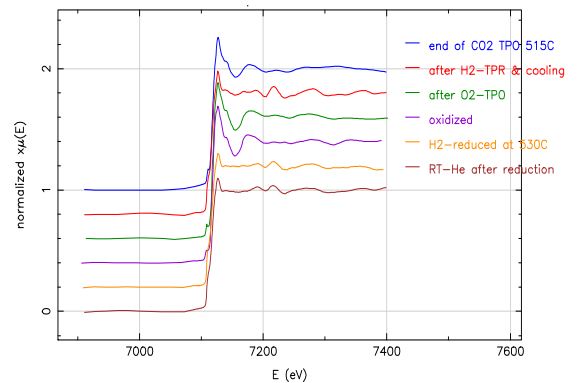


**Figure 2**: XAS scans over the catalyst  $Fe_2O_3/CeO_2$ ; left:  $H_2$ -TPR ; right:  $CO_2$ -TPO after the  $H_2$ -TPR.

A comparison of several treatments on the catalyst  $Fe_2O_3/CeZrO_2$  is shown in figure 3. Switching of the Fe oxidation state between reduced and oxidised is obvious. At first sight, the Fe state in the catalyst changes between 3+ and 0. Further investigation is needed to determine the exact oxidation state, the influence of the matrix  $CeZrO_2$  compared to  $CeO_2$  and the possible influence of repeated redox cycles on the local environment of Fe.

### Conclusions

First results have been obtained on 3 iron oxide catalysts with different hosts and their respective behaviour in redox experiments. A more detailed investigation will require careful preparation of homogeneous samples to improve data quality and avoiding vertical beam displacement, for which adjustment is underway.



**Figure 3**: XANES for catalyst  $Fe-CeZrO_2$  following several redox treatments.