



	Experiment title: Hydrogen production over iron oxide catalysts: in situ XAS investigation of the iron oxide reduction/oxidation behaviour	Experiment number: 26-01-910
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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, Fe₂O₃, Fe₂O₃/CeZrO₂ and Fe₂O₃/CeO₂, 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 O₂ and CO₂. Several iron oxides, FeO, Fe₂O₃, Fe₃O₄, as well as Fe foil were measured as reference oxidation states.

Results

The 3 catalysts Fe₂O₃, Fe₂O₃/CeO₂ and Fe₂O₃/CeZrO₂ 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 Fe₂O₃ and Fe₃O₄ (Fig. 1 right). Best correspondence exists with the signal of Fe₂O₃, indicating that the Fe is essentially in a 3+ state with ferric oxide structure.

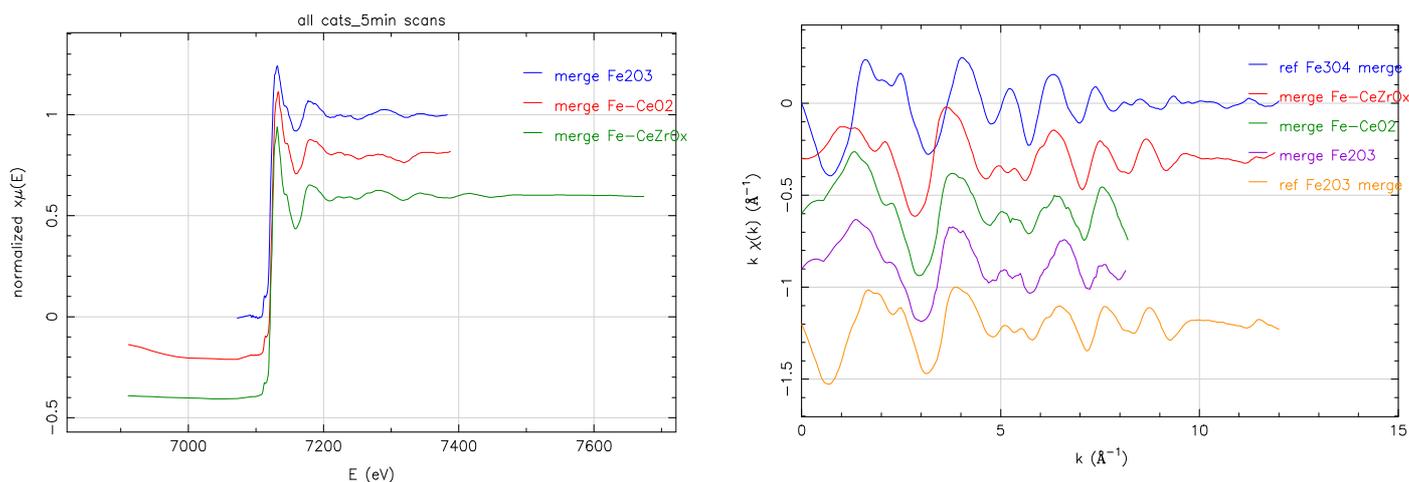


Figure 1 : left : normalised absorption signal for the 3 catalysts, Fe_2O_3 , Fe_2O_3/CeO_2 and $Fe_2O_3/CeZrO_2$; right: k -weighted EXAFS signal for the 3 catalysts and for powder references Fe_2O_3 and Fe_3O_4 .

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.

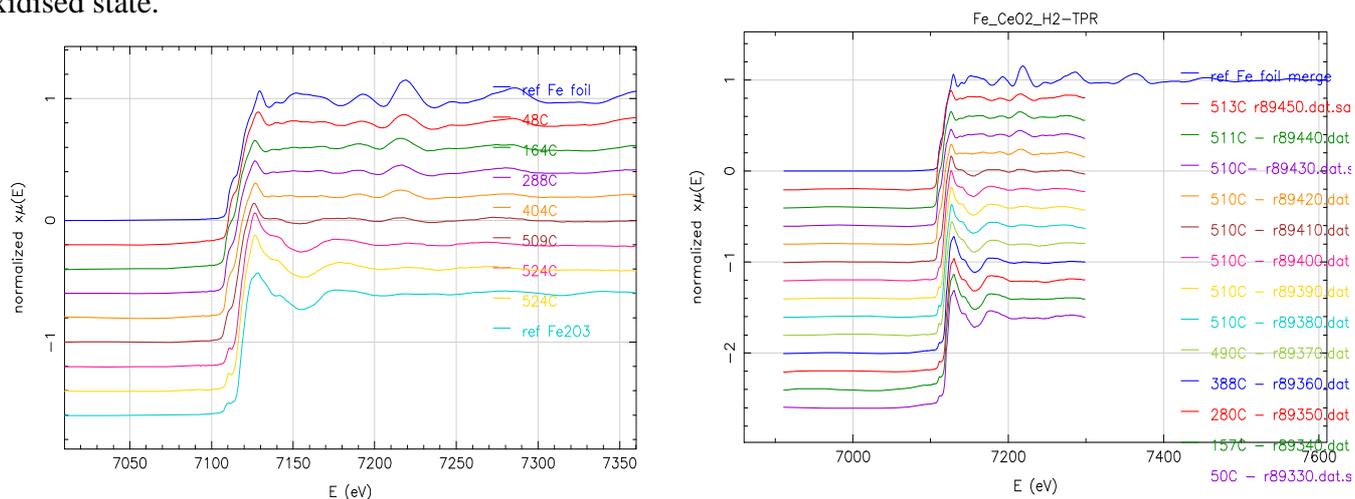


Figure 2: XAS scans over the catalyst Fe_2O_3/CeO_2 ; left: H_2 -TPR ; right: CO_2 -TPO after the H_2 -TPR.

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.

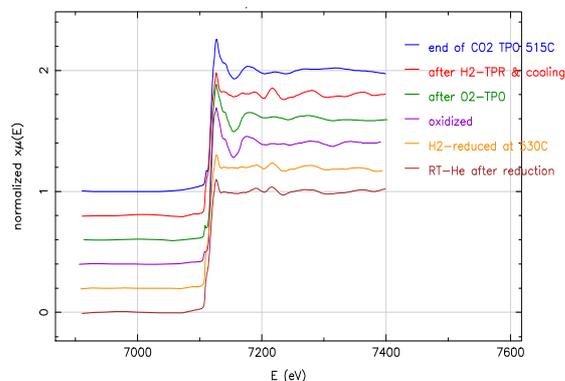


Figure 3: XANES for catalyst $Fe-CeZrO_2$ following several redox treatments.