DUTCH-BELGIAN BEAMLINE AT ESRF

EUROPEAN SYNCHROTRON RADIATION FACILITY

Experiment Report Form

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.

(next page)

DUBBLE	**Experiment title:** Combined XAFS/WAXS study of promoted iron Fischer-Tropsch Catalysts	**Experiment number**: **26-01-788**
Beamline: BM26A	**Date(s) of experiment**: From: 04-10-2007 To: 09-10-2007	**Date of report**: 12 - 10 - 2007
Shifts: 15	**Local contact(s)**: Dr Sergey NIKITENKO (e-mail: nikitenko@esrf.fr)	

Names and affiliations of applicants (* indicates experimentalists):

Emiel de Smit, dr. Frank de Groot, Ad van der Eerden, Prof.dr. Bert Weckhuysen, Department of Inorganic Chemistry and Catalysis, Utrecht University, The Netherlands

Experimentalists

Emiel de Smit*, Dr. Andy Beale*, Elena Sacaliuc*, Dr. Ana Iglesias Juez*, Department of Inorganic Chemistry and Catalysis, Utrecht University, The Netherlands

Report: (max. 2 pages)

This beamtime was a continuation of a previous beamtime (26-01-779: XANES and EXAFS study of the activation and deactivation of Fe-based Fischer-Tropsch Catalysts). During the present beamtime, work was focused on gaining insight into the iron phases present in Fe-based Fischer-Tropsch (FT) catalysts under working conditions. Therefore, the main part of the time was spent on collecting *in situ* XAFS/WAXS data during the activation and reaction of the catalysts. The remainder of the time was spent on an *in situ* study of phase changes during heating to 450^{o}C in CO/H_2 mixtures at higher temperatures and *ex situ* collection of XAFS/WAXS data on standard reference compounds.

XAFS/WAXS study of the Fe-based Fischer-Tropsch catalysts

Three different Fe-based catalysts; bulk α-Fe_2O_3, Fe_2O_3/CuO and $Fe_2O_3/CuO/K_2O/SiO_2$, were studied under identical conditions. The catalysts were pretreated at 350^{o}C in a pure H_2 while WAXS and XANES data were recorded continuously. After the pretreatment, EXAFS data was recorded using the quick EXAFS mode. The FT reaction was performed at 250^{o}C while flowing CO/H_2. XANES and WAXS data was recorded continuously while the reacting gases and evolving reaction products were monitored using an on-line mass spectrometer. After 4 h FT reaction time, EXAFS data was collected in the quick EXAFS mode.

During the different stages of the catalyst lifetime (pretreatment, reaction, end of run), significant changes were observed in the XANES and WAXS data (Figure 1). After pretreatment, the bulk α-Fe_2O_3 and Fe_2O_3/CuO catalysts were almost completely reduced to metallic iron, while the $Fe_2O_3/CuO/K_2O/SiO_2$ sample was only partially reduced. During reaction, metallic iron was quickly converted to a mixture of iron carbides and iron oxide (magnetite). The different catalysts showed subtle differences in the kind of carbides formed, leading to differences in catalytic behavior.

Overall, the quality of the recorded XAFS and WAXS data was very good and many valuable insights were gained into the catalytic system. It is to be expected that the results will be published in open literature in due time.

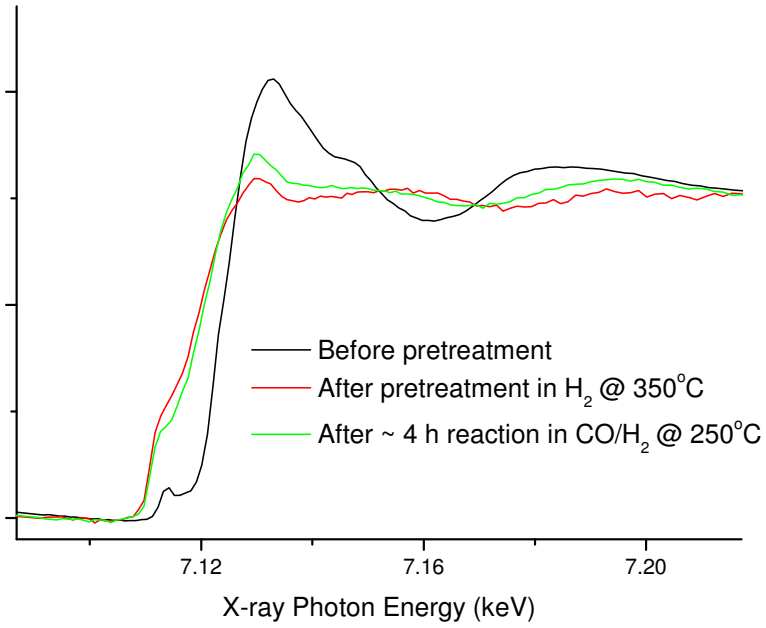

Figure 1: XANES spectra of the Fe_2O_3/CuO catalyst before reaction (black) and after pretreatment (red) and after ~ 4 h of reaction time (green).

In situ study of phase changes during heating in CO/H_2 mixtures

The same three catalysts that were used in the *in situ* reaction study: bulk α-Fe_2O_3, Fe_2O_3/CuO and Fe_2O_3/CuO/K_2O/SiO_2, were further examined by slowly heating them up to 450°C in a flow of H_2/CO gas. Gradual changes were observed in the XANES and WAXS data, as the iron oxide starting material was slowly carburized into a mixture of metallic iron and iron carbides. Some graphite was observed to form at higher temperatures. The data on the distinct carburization behavior of the different catalysts gives valuable information on the system and it is to be expected that these results will be published in due time.

Conclusions

By applying the experience from past beamtimes (26-01-779), the present experiments yielded valuable results and important new insights into the catalytic system. Overall, the user support on the beamline was outstanding once again.