ESRF	**Experiment title:** **The accurate crystal structure and role of Haegg Carbides during *in situ* Fischer-Tropsch synthesis**	**Experiment number:** CH3027
Beamline: ID31	**Date of experiment:** from: 03/02/2010 to: 05/02/2010	**Date of report:** 12/03/2010
Shifts: 9	**Local contact(s):** Dr Caroline Curffs	*Received at ESRF:*

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Report:

During experiment CH-3027 the crystal structure of Haegg carbide (χ-HC) formed *in situ* Fischer-Tropsch synthesis at 2 MPa and 330 °C was determined. χ-HC is generally accepted to be responsible for FT synthesis activity (and not the metallic iron) [1-3], but some controversy as to the exact structure of the carbide under Fischer-Tropsch synthesis conditions still persists, partly due to the small crystallite size of the carbide [4-6] which makes structure determination by conventional means difficult. Rietveld and radial distribution function analyses of an *ex situ* high resolution powder XRD of a χ-HC sample indicated the bulk crystal structure of this phase to extend to the surface. It is known that surface restructuring of catalyst surfaces could be induced by reactor gas and temperature [7]. To determine the exact crystal structure and possible surface modification of χ-HC *in situ* under FT conditions a XRK600 Anton Paar reaction chamber was coupled to the high resolution diffractometer at ID31 (Fig 1) and a high resolution *in situ* powder diffractogram measured at the time of maximum χ-HC relative abundance in the catalyst.

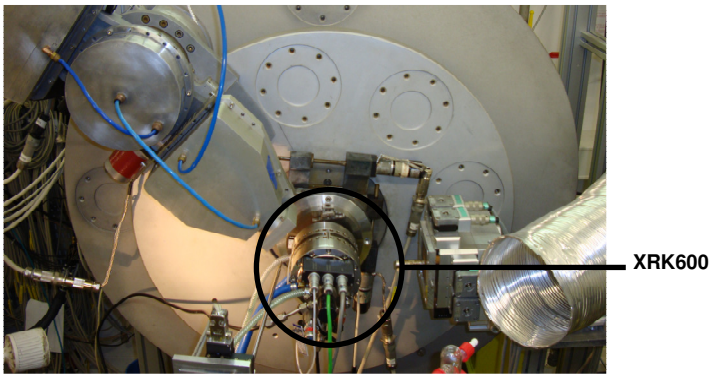

Figure 1: Connection of modified XRK600 to ID31 diffractometer

Aluminium powder was used for temperature calibration of the reaction chamber [8].

χ-HC was then prepared and analyzed *in situ* by reacting a model iron catalyst with syngas under FTS conditions as follows. The model iron catalyst powder was packed in the reaction chamber and the chamber was then purged with syngas (H_2:CO=2) at room temperature to remove air. The gasflow was directed through the catalyst bed to maximize conversion. The gas pressure in the chamber was increased to and maintained at 20 MPa with a continuous flow of syngas at 75 ml/min through the catalyst bed during this experiment. The temperature of the reaction chamber was then increased from room temperature to 330 °C at 10 °C /min, whilst collecting diffractograms to follow the reaction of iron with syngas to form χ-HC.

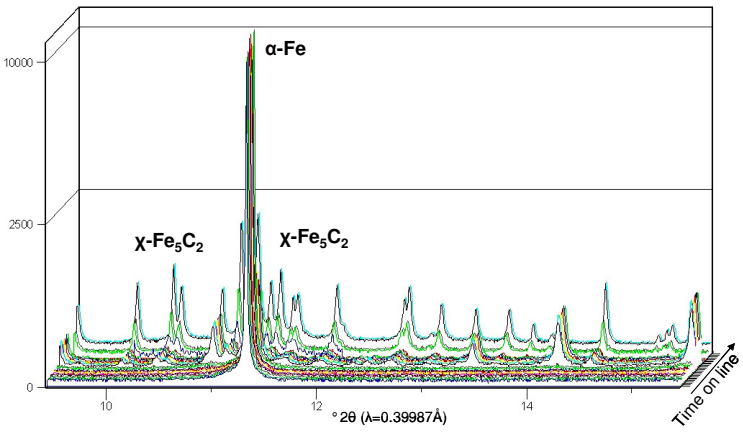

Figure 2: Evolution of phases during reaction at 2000 kPa

In situ high resolution powder diffractograms obtained at beam line ID31 during experiment CH-3027 indicated the transformation of ferrite (α-Fe) to χ-HC at 20 MPa and 330 °C when exposed to syngas.

Quantitative phase determination by Rietveld analysis of the *in situ* high resolution diffractogram obtained, indicated the sample to contain 85 weight % χ-HC (with average crystallite size of 98 nm) and 15 weight % cementite. It is the first time that χ-HC was prepared and measured *in situ* as a phase present during Fischer-Tropsch synthesis using high resolution powder XRD. The results will be correlated with catalyst activity and selectivity.

References

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