	Experiment title: The accurate crystal structure and role of Haegg Carbides during <i>in situ</i> Fischer-Tropsch synthesis	Experiment number: CH2702
Beamline: ID31	Date of experiment: from: 25/02/2009 to: 28/02/2009	Date of report: 29/04/2009 <i>Received at ESRF:</i>
Shifts: 9	Local contact(s): Dr Andy Fitch	
Names and affiliations of applicants (* indicates experimentalists): E du Plessis (Sasol, South Africa)* A Ferreira (Sasol, South Africa)* M Rayner (University of Witwatersrand, South Africa)* A Steuwer (Lund University, Sweden; NMMU, South Africa)*		

Report:

During experiment CH-2702 it was attempted to accurately determine the crystal structure and stability of Haegg carbide (χ -HC) during *in situ* Fischer-Tropsch synthesis at 2 MPa and 330 °C. 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. Unfortunately, the reactor set-up during experiment CH-2702 for the *in situ* catalysis (Figure 1) could only reach 500 kPa at 330°C due to failure of the quartz capillaries and insufficient temperature resistance of the glue. The highest pressure obtained at 330°C was 500 kPa and under these conditions only 40 weight % of χ -HC could be obtained. Previous work done (Figure 2) on a laboratory diffractometer showed that at 2 MPa concentrations of χ -HC up to 80 weight % could be obtained.

During the experiment CH-2702 several improvements were made on the initial *in situ* reactor set up, such as using sapphire capillaries. Further optimization of the reactor is necessary to reach and maintain the syngas pressure at 2 MPa at high temperature as well as to calibrate and control gas flowrates. The local atomic structure of χ -HC could thus not be determined through PDF analyses. The relative abundances of crystalline phases obtained at 500 kPa were significantly different (Figure 3) from those obtained in the laboratory experiment performed at 2 MPa (Figure 2) and indicates that the syngas pressure determines the stability of χ -HC.

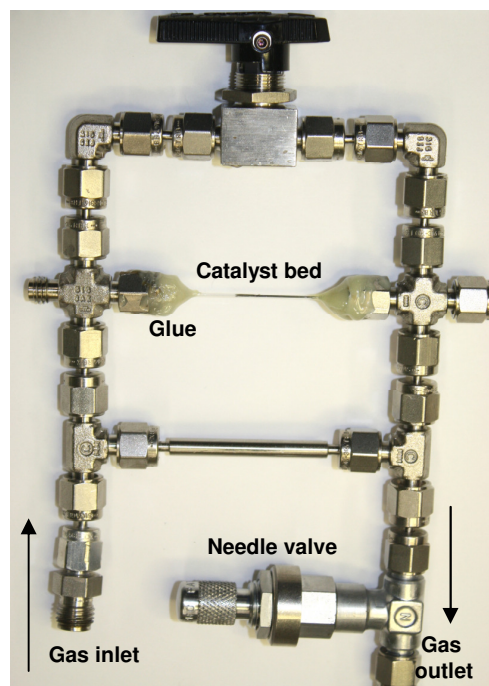


Figure 1: *In situ* reactor setup

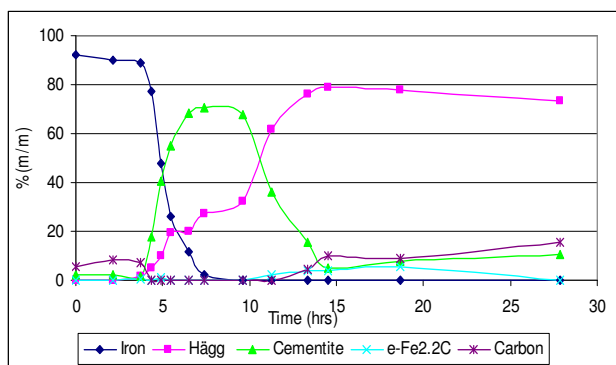


Figure 2: Evolution of phases during reaction at 2 MPa

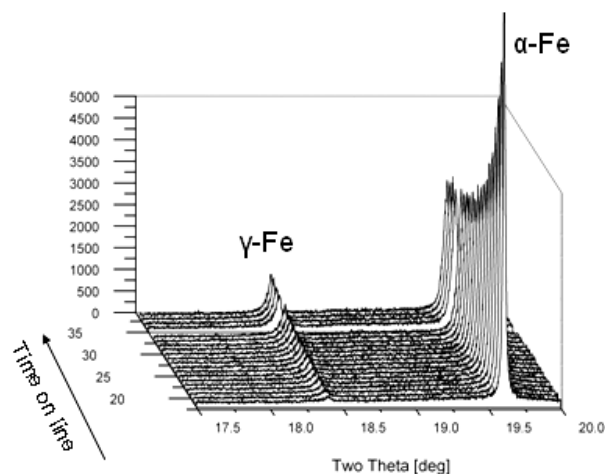


Figure 3: Evolution of phases during reaction at 500 kPa

From a laboratory *in situ* XRD experiment it is known that activated, unpromoted iron catalyst contains mainly ferrite (α -Fe), which reacts at 2 MPa and 330 °C with syngas to form mixtures of cementite (Fe_3C), χ -HC and ferrite (α -Fe) (Figure 2). *In situ* high resolution powder diffractograms obtained at beam line ID31 during experiment CH-2702 indicated the transformation of ferrite (α -Fe) to austenite (γ -Fe) and χ -HC at 5 bar and 330 °C when exposed to syngas. Ferrite has a bcc structure and austenite is fcc. Austenite displays a characteristic silver-white in pure form, as was observed during experiment CH-2702 (Figure 4).

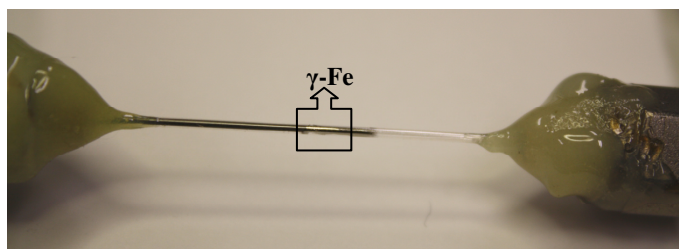


Figure 4: Catalyst bed post FTS

Austenite is not generally known for being an FT active phase. From the Fe-C phase diagram ferrite (α -Fe) is the predominant phase at temperatures lower than 738 °C and carbon concentrations less than 2 mass %. Both ferrite (α -Fe) and austenite (γ -Fe) are stable at temperatures exceeding 738 °C and these phases form cementite and austenite with increasing carbon concentration. The larger phase field of austenite compared with that of ferrite on the Fe-C phase

diagram indicates the greater solubility of carbon in austenite (the maximum is 2.08 mass % at 1154 °C). It is the first time that austenite was identified as a phase present during Fischer-Tropsch synthesis. The results will be correlated with catalyst activity and selectivity.

References

- [1] Dry, M. E., Catalysis Letters 7 (1990) 241-252.
- [2] Riedel, T., Schulz, H., *et al.*, Topics in Catalysis, 26, 1-4, 2003, 41-54.
- [3] Niemantsverdriet, J. W.; *et al.*, J. Phys. Chem. 84 (1980) 3363-3370.
- [4] Hagg, G., Z. Physic. Chem. B12 (1931) 33-56.
- [5] Retief, J. J., Powder Diffraction 14 (1999).130-132.
- [6] Senateur, J. P.; *et al.*, Comptes Rendus Acad. Sci. 255 (1962) 1615-1616.