

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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.



	Experiment title: X-ray absorption spectroscopy for the study of a chromium homogeneous catalysis system for selective trimerisation of ethene.	Experiment number: CH-2125
Beamline: BM26A	Date of experiment: from: 12 Dec 2005 to: 16 Dec 2005	Date of report: 30 Aug 2006
Shifts: 9	Local contact(s): Dr Sergey Nikitenko	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): John EVANS,* Jerome MOULIN,* Gillian REID,* Moniek TROMP* School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK Dr David McGuinness* Sasol Technology (UK) Ltd, Purdie Building, North Haugh, St Andrews, Fife, KY16 9ST, UK		

Report:

The selective conversion of ethene to higher alkenes is a process of significant importance. Present technology is based on a restricted polymerisation process (oligomerisation) and this affords a distribution of the formula $(C_2H_4)_n$ which can be modified by alkene metathesis. Direct methods to specific alkenes would be both commercially and environmentally desirable. Two important alkenes are 1-hexene and 1-octene. Each are important chemical intermediates for the manufacture of materials such as surfactants and polymers. A series of early transition complexes have been found to be effective catalyst precursors, and the mechanism proposed differs from the chain growth via insertion of alkenes into a M-C bond. Rather, the key step involves the oxidative coupling of two coordinated alkenes to form a metalacyclopentane.¹

A series of these precursors are of the type $CrCl_3(L_3)$, where L_3 may be a tridentate ligand, or a bidentate ligand with a labile solvento ligand occupying the 6th coordination site on an octahedron. Mechanisms for selective oligomerisation have been proposed based on Cr(II/IV) and Cr(I/III) cycles. Depending upon the nature of the ligand, catalysis may effect selective trimerisation ($L_3 = \{NH(CH_2CH_2S-C_{10}H_{21})_2\}$), tetramerisation ($L_3 = NR(PPh_2)_2 + THF$) or polymerisation (e.g. $L_3 = E(CH_2CH_2S-C_{10}H_{21})_2$ }, $E = O$ or S). So a programme of Cr K-edge XAFS studies were carried out on these systems to address two questions:

- 1) What is the coordination sphere of the catalysts activated by aluminium reagents and
- 2) Can the oxidation state of the metal be established from the XANES patterns of these complexes?

XAFS spectra on a series of chromium complexes of different oxidation states, geometry and ligand sets were recorded on BM26A, which afforded spectra of good resolution and signal/noise. The normalised XANES of a selection of these complexes is shown in Figure 1.³ These spectra are rich in detail and show a generally increasing trend with oxidation state. These complexes are predominantly with hard donor ligands.

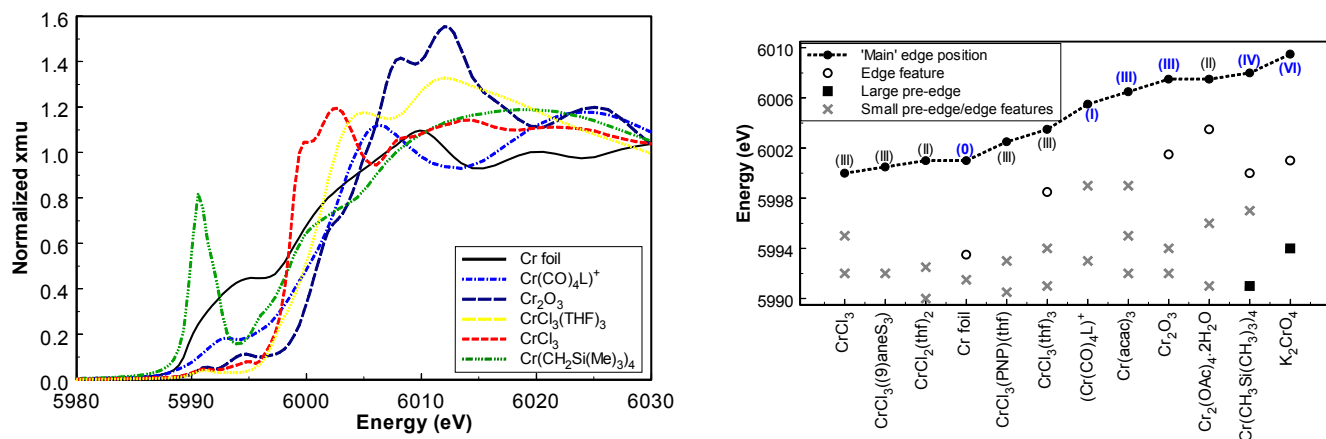


Figure 1. Left: Cr K-edge XANES of a selection of chromium complexes of different oxidation states; Right a plot of the energy of the spectral features.

The catalyst precursors of the type CrCl₃(L)₃ however contain a mixture of hard and soft donor ligands and in an octahedral geometry can adopt *fac* and *mer* isomers. Figure 2 shows a plot of the main edge position of these and related Cr(III) complexes. These show almost the same range of positions as in Figure 1 which spans up to Cr(VI). Two observations appear clear: (i) there is a significant (8 eV) edge shift on changing from a chloride ligand environment to one of oxygen donors and (ii) there is a distinction in the behaviour of *fac* and *mer* complexes of the type CrCl₃(L)₃. The *fac* isomers show little variation with the nature of the tridentate ligand, whilst the *mer* isomers show a higher energy position for the edge (up to 4 eV) and a larger variation. So an estimated mean edge position for a mixed ligand set would not be appropriate if there were a change in geometry. These results show that much care should be applied when seeking to establish an oxidation state for a complex of unknown geometry.

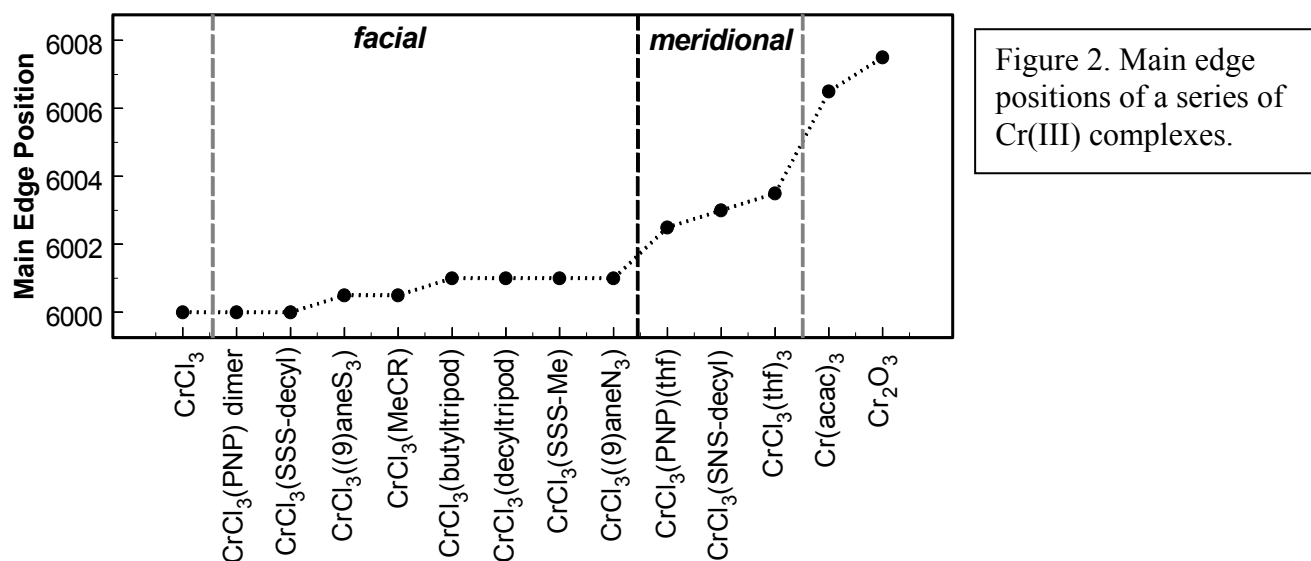


Figure 2. Main edge positions of a series of Cr(III) complexes.

References

1. Yu, Z. and Houk, K. N.; *Angew. Chem. Int. Ed.*, (2003), **42**, 808.
2. Bollman, A., Blann, K., Dixon, J.T., Hess, F.M., Killian, E., Maumela, H., McGuinness, D.S., Morgan, D.H., Neveling, A., Otto, S., Overett, M., Slawin, A.M.Z., Wasserscheid, P., and Kuhlmann, S.; *J. Amer Chem Soc*, (2004), **126**, 14712.
3. Tromp, M., Moulin, J., Reid, G., and Evans, J.; *Proceedings of XAFS13*, Stanford University, 2006.