

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 via the User Portal:

<https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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: In operando XAFS investigation at Cl K-edge and Ir L3-edges of a hydrogen transfer Ir catalyst immobilised on Wang's resin	Experiment number: CH-4055
Beamline: BM28	Date of experiment: from: 18/06/2014 to: 24/06/2014	Date of report: <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Paul Thompson	
Names and affiliations of applicants (* indicates experimentalists): Dr Bao N Nguyen, University of Leeds* Dr Mark Newton, ESRF Dr Richard Bourne, University of Leeds Dr Patrick McGowan, University of Leeds Prof. A. John Blacker, University of Leeds Dr Thomas Chamberlain, University of Nottingham* Michael Chapman, University of Leeds* Grant Sherborne, University of Leeds*		

Report: The experiments aimed to investigate the structure of immobilised Cp^*IrCl_2 catalysts on polystyrene and their deactivation under catalytic conditions. Three questions were identified in the proposal, and their answers/outcomes from our experiments are summarised below. The results of these experiments are being prepared for a manuscripts for *Angew. Chem. Int. Ed.* within the next month.

Q1: *The structure of the catalyst before, during and after multiple uses and after reactivation with aqueous HCl wash.*

Probing structural information on immobilised homogeneous catalysts is a challenge using lab-based techniques, due to interference from the support material. XAFS has been employed for decades to study heterogeneous catalysts in bulk chemical processes. Applications in fine chemical context, however, are few.

XANES spectra of a number of solid samples were measured in fluorescence mode at the Cl K-edge and room temperature. The results were consistent with previous measurement in 4-bunch mode and suggested a steady loss of Cl content between the fresh and the deactivated catalysts. Significant changes to the normalised spectra, however, were not confidently detected, showing at least little changes to the coordination environment of the remaining chloride, *i.e.* it is still in an Ir-Cl bond (Fig. 1a and 1b).

These findings are consistent with Ir L-edge EXAFS data collected at B18, Diamond Light Source, which showed loss of the Ir-Cl signal as the catalyst was deactivated (Fig. 1c). Importantly, the fresh catalyst showed less intensity of the Ir-Cl signal compared to that of $[\text{Cp}^*\text{IrCl}_2(\text{pyridine})]$, and much less than that of the $[\text{Cp}^*\text{IrCl}_2]_2$ dimer (which has three Ir-Cl bonds for each Ir atom) (Fig. 1d). Consequently, it was concluded that the immobilised catalyst was in monomer form, in spite of its dimeric state before immobilisation. The small decrease in Ir-Cl intensity compared to $[\text{Cp}^*\text{IrCl}_2(\text{pyridine})]$ was attributed to a small extent of ligand exchange during washing post immobilisation.

Q2: *The influence of the linker length on the structure of the catalyst.*

Our previous work has shown that a longer linker, *i.e.* $(\text{CH}_2)_{14}$, leads to comparable catalytic activity to that of the homogeneous catalyst. A shorter linker, *i.e.* $(\text{CH}_2)_5$, results in a significant decrease in catalytic activity, which is likely due to poor mass transfer of the reactants to the immobilised catalyst on the resin. On

the other hand, the immobilised catalyst with long linker was deactivated after 3 uses while the catalyst with short linker can be reused upto 30 times. Understanding the possible difference in their deactivations is therefore essential in developing new immobilised catalysts with improved activity and stability.

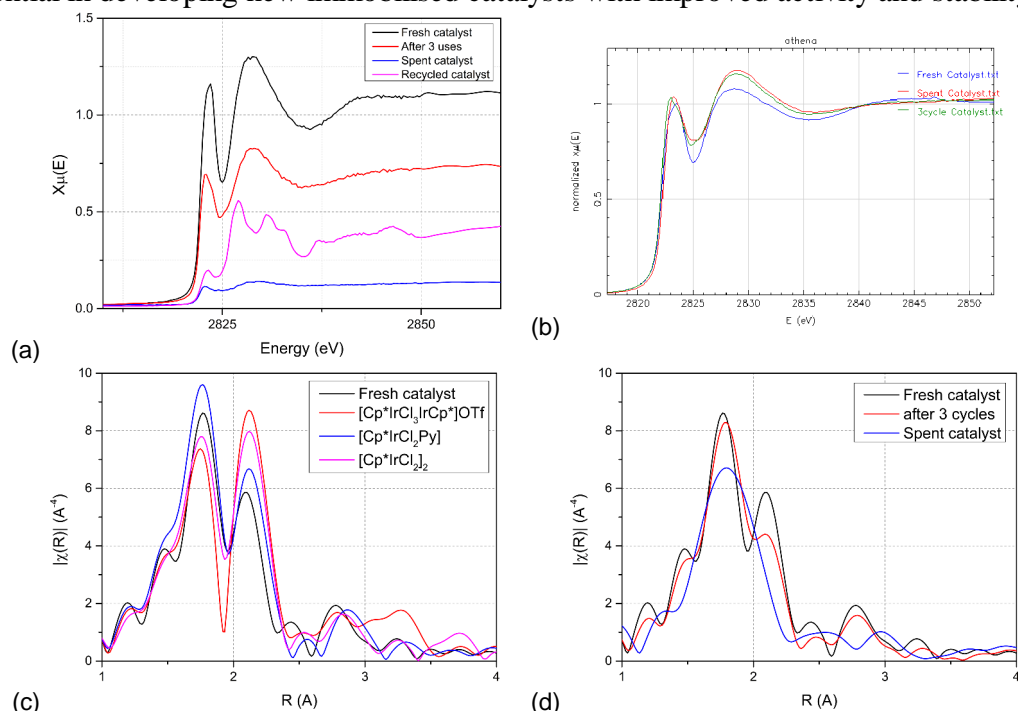


Figure 1. Cl K-edge XANES (a) and (b) and Ir L-edge EXAFS spectra of the immobilised catalysts (c) and (d)

Ex situ samples of the two deactivated catalysts, with C14 and C5 linkers, were compared using Cl K-edge XANES. To our surprise, the spectra of the two samples are very similar with low Cl content and XANES features (Fig. 2a). These results were corroborated by Ir L-edge EXAFS data (Fig. 2b). The two catalysts are therefore likely deactivated through a similar mechanism which leads to the loss of chloride. The accelerated deactivation observed with the longer linker may be intrinsic to the more 'homogenous' nature of the catalyst. Consequently, the solution to combine its higher catalytic activity with robustness will have to be found in methods which can suppress catalyst deactivation.

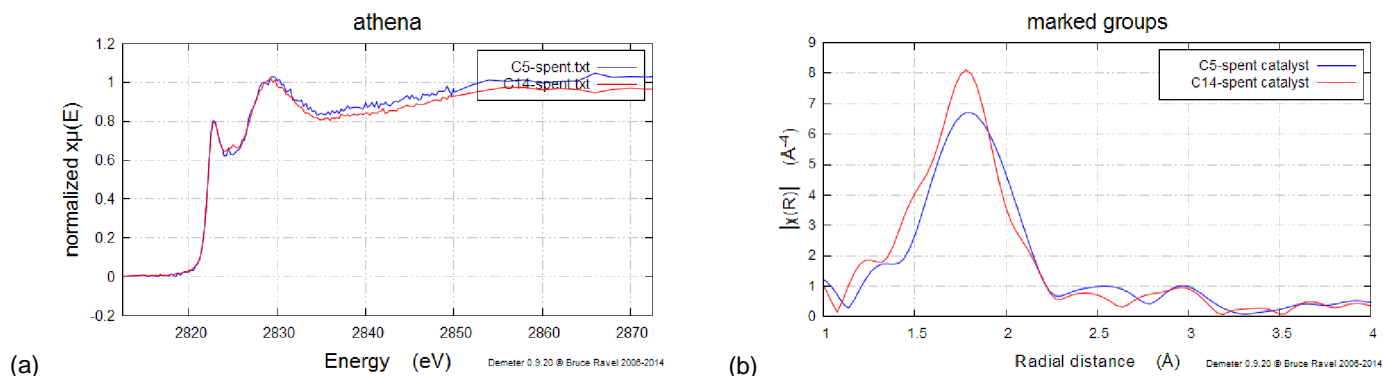
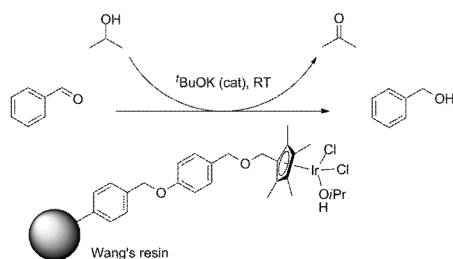


Figure 2. Normalised Cl K-edge XANES (a) and Ir L-edge EXAFS spectra of C5 and C14 deactivated catalysts

Q3: The structure of the catalyst during turnover.

Understanding the mechanism of transfer hydrogenation using the immobilised catalysts and their deactivation pathway is a key objective of the study, as it will enable us to rationally design more active and robust catalysts for industrial applications. Consequently, an *in situ* experiment was performed, where in the reaction solution was flowed over the immobilised catalyst at 60 °C. XANES and EXAFS spectra were collected on the catalyst (through a 50 μm thin film of liquid and a 6 μm polypropylene window) in fluorescence mode (Scheme 1).

Our XANES spectra of the solid samples suggested the loss of chloride from the catalyst. We deduced that this was due to replacement of chloride by alkoxides as ligand on the Ir cation. Complete exchange of chlorides would result in a deactivated species such as $[\text{Cp}^*\text{Ir}(\text{OR})_3]^+$, which requires a positive counterion. Under the reaction conditions, this is likely to be K^+ (from the base KO^tBu). Consequently, XANES spectra at K K-edge data were collected in addition to and Cl K-edge XANES and Ir L-edge EXAFS spectra.



Scheme 1. *In operando* XAFS experiments in a flow-cell (right side, with a 2 mm dia. window)

The results at were very insightful regarding the activation and deactivation of the immobilised catalyst. Treatment of the immobilised catalyst with KO^iBu quickly led to the loss of 50% of the chloride content and a small increase in the potassium content. This is consistent the exchange of one chloride ligand on the Ir catalyst with an alkoxide as an activation step to generate the active catalyst (Fig. 3). Similar activation steps have been proposed previously, but this is the first concrete spectroscopic evidence supporting such proposal.

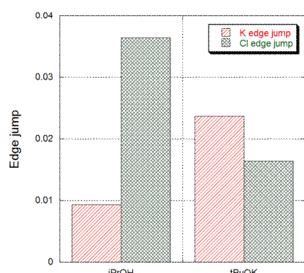


Figure 3. Changes to Cl and K content during activation of the catalyst

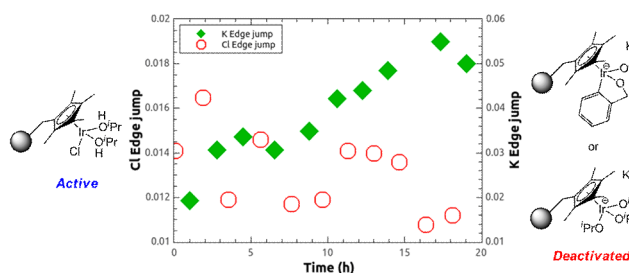
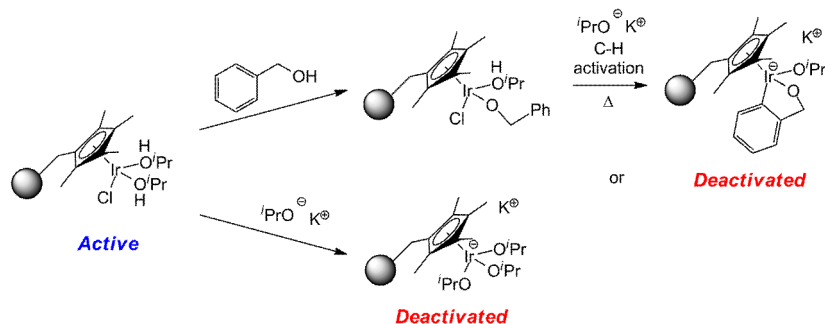


Figure 4. Changes in Cl and K content of the immobilised transfer hydrogenation catalyst over time in continuous reaction mode

proposed deactivation pathway (Fig. 4). Association of these changes to the decrease in catalytic activity is being finished in our lab. Preliminary results, however, confirmed that catalytic activity also steadily decreases during a similar time period. These changes could be explained by two possible structures of the deactivated catalysts, being formed through ligand exchange between alkoxides and chloride or a C–H activation of the benzyloxy ligand (Scheme 2).



Scheme 2. Possible deactivation pathways

Ir L-edge EXAFS data in this *in situ* experiment, however, were of insufficient quality to evaluate the changes around the coordination sphere of Ir. This was partially due to significant fluorescence signal from the stainless steel flow-cell, which overwhelmed our detector. Filtering these off led to significant decrease in Ir L-edge signal to noise. Solutions to this will be incorporated into our next flow-cell design.

Conclusions: The study was successful in solving the following questions regarding the nature of the catalysts and its state during catalytic reaction:

- The structure of the immobilised catalyst (dimer vs monomer) was determined to be monomer.
- The activation of the catalyst with organic base was found to remove one chloride ligand from the iridium pre-catalyst.
- The deactivation of the catalyst was associated with a steady loss of chloride and an increase of potassium content.

The study has also demonstrated the capability of a multi-element XAFS approach in delineating multiple changes of the immobilised catalyst through different stages of the catalytic reaction. The results have led to a number of possible methods to reactivate the catalyst or to suppress catalyst deactivation, which will be the subject of a follow-up study.