



Experiment title: Reactivation and Suppression of Deactivation of An Immobilised Cp*IrCl₂ Catalyst for Robust Industrial Transfer Hydrogenation

Experiment number:
28-01-1091

Beamline:
BM28/
XMaS

Date of experiment:
from: 10 June 2015 to: 16 June 2015

Date of report:

Shifts: 18

Local contact(s): Paul Thompson

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

Bao N. Nguyen*, University of Leeds

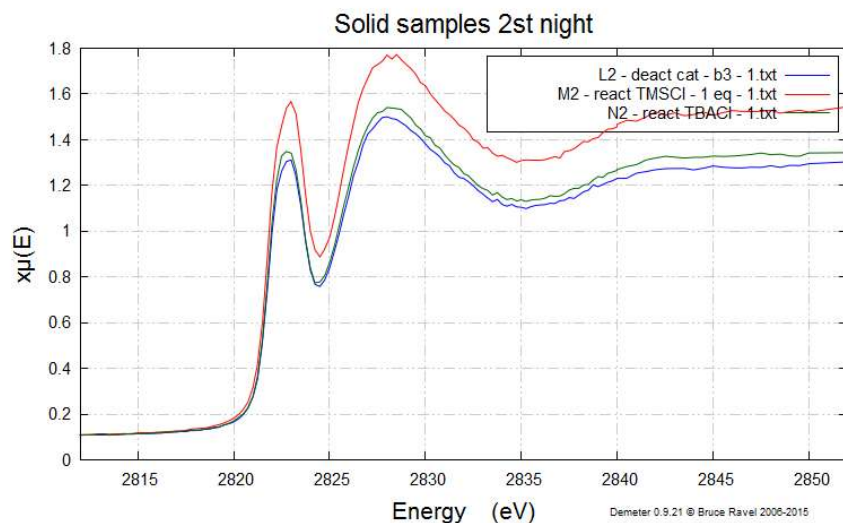
Patrick McGowan, University of Leeds

Richard Bourne, University of Leeds

John Blacker, University of Leeds

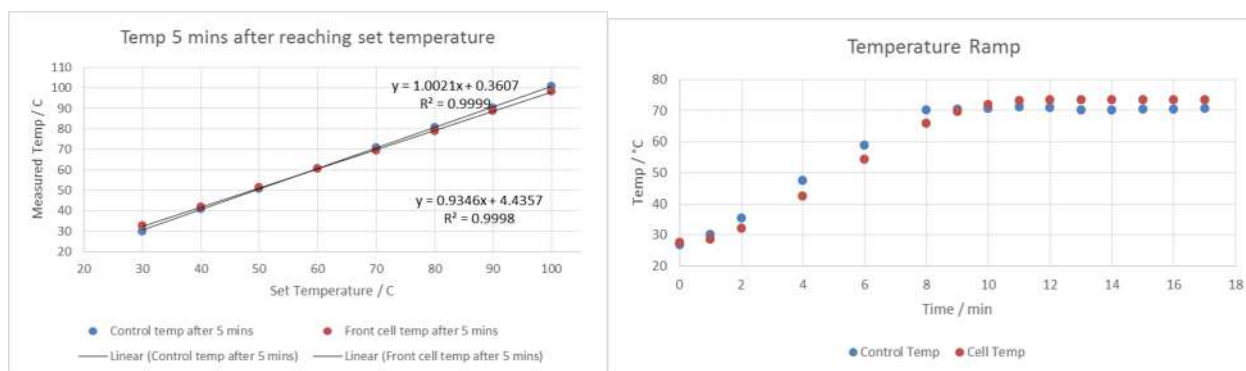
Report: The experiment was conducted through a series of solid samples and in situ experiments using a spectroscopic flow-cell. XANES spectra were collected at Cl K-edge and were analysed using the Athena software of the Demeter package. Raw data from the beamline was extracted and combined for each scan using Python.

A series of possible reactivation methods were developed in our lab, based on findings of experiment CH4055. The aim of this study is to compare the Cl K-edge XANES spectra of these reactivated samples with the deactivated catalyst, in addition to Ir L-edge data collected at B18, Diamond Light Source.

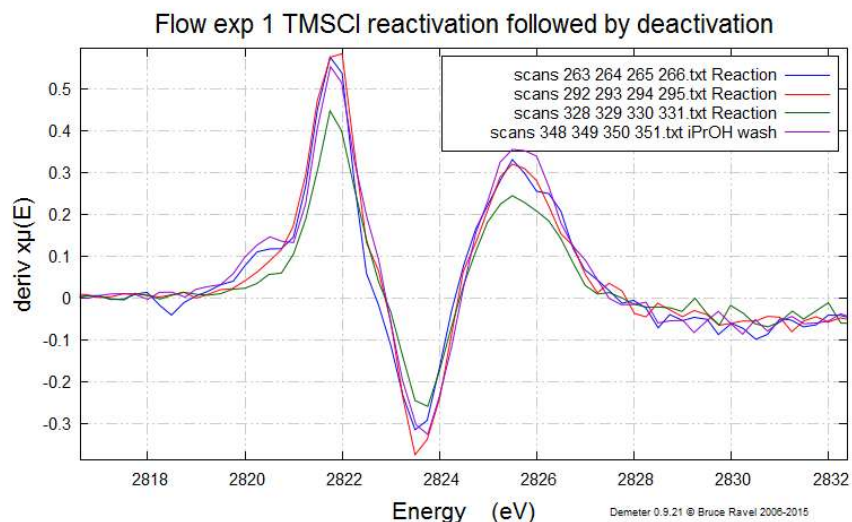
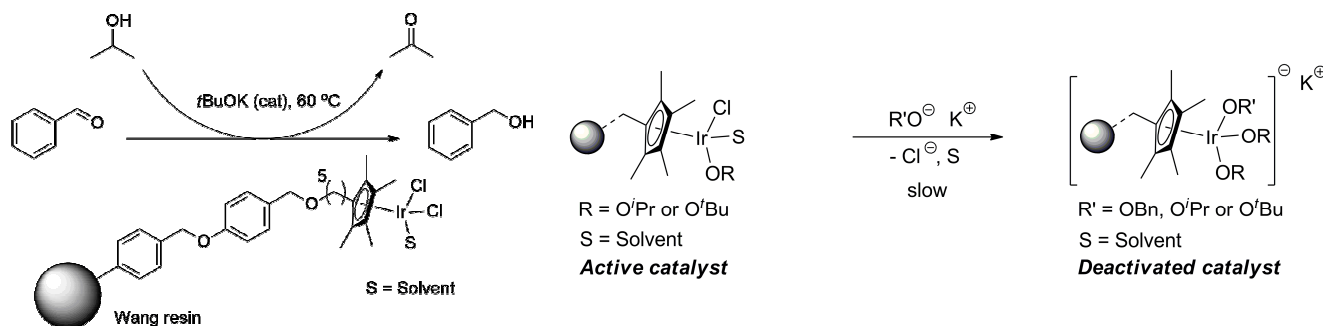


Data from solid samples suggested TBACl treatment having little effect on the partially deactivated catalyst. However, TMSCl treated catalyst (1 equivalent of TMSCl per Ir) showed an increase in Cl content (10-15%).

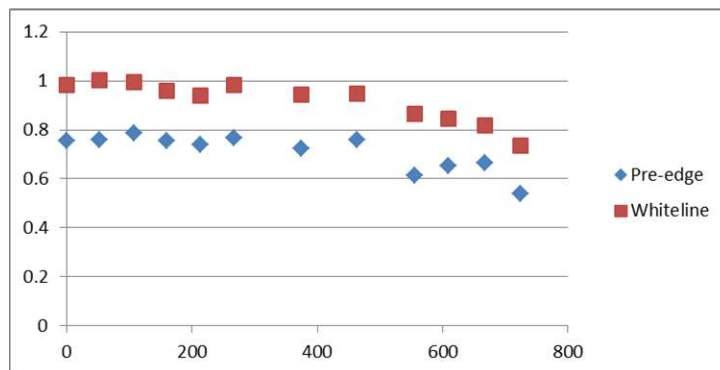
An *in situ* experiment was consequently performed using the same flow-cell from our previous study ([DOI: 10.1021/ja512868a](https://doi.org/10.1021/ja512868a)). Temperature calibration of the flow-cell was acceptable with a maximum 1-minute lag between set temperature and measured temperature at the catalyst bed.



Treatment of the partially deactivated catalyst with a pulse of TMSCl led to the development of a new shoulder in the pre-edge feature, which slowly dissipated upon treating with the reaction mixture.



The Cl content, after reactivation with TMSCl , slowly decrease as expected upon treatment with reaction mixture, as demonstrated in the plot of pre-edge and whiteline vs time below. This is the expected for such catalyst reactivation/deactivation.



The process was repeated with other 'reactivation' methods using HCl and TBACl. Both of these have been found to be less effective in reintroducing the Cl ligand in the coordination sphere of iridium.

Kinetic experiments to correlate these findings with the measured catalytic activity and structural studies in our lab is in progress with an anticipated publication within 12 months.