

Soft X-ray absorption spectroscopy studies of Cl containing organometallics and catalysts.

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Summary

Using the “4 bunch” mode of the ESRF we have investigated the potential of XMaS to provide a viable resource for the study of materials and their behaviour from the perspective of “soft” K edges such as Cl and 4d transition metal L₃ edges edges such as Rh.

Our preliminary results show that XMaS can provide a highly useful resource for studies of this nature (which span disciplines from physics, and materials science to chemistry and biology), and one that may yet be further optimised. We note that resources actively dealing with this spectroscopic energy regime are in some deficit worldwide.

Introduction.

The state, whereabouts, and function of elements such as P, S, and Cl in both homogeneous and heterogeneous catalysis is relatively poorly understood: this situation goes well beyond catalysis these elements being ubiquitous in many areas of soft condensed matter, geosciences, and biology.

In many catalyst formulations these elements may be found and are well known to modify the nature and performance of these materials in both advantageous and deleterious ways: sulphur and phosphorous are for instance well known poisons in the petrochemical and automobile exhaust arenas.

In the current cases Cl has been shown to influence the atomic dispersion of Rh, catalytic reactivity, and has been long implicated in the oxidative disruption of small Rh nanoparticles by gases such as CO. Yet the details of how and why this happens remain largely unknown as suitable probes to study these effects are few and far between.

Cl is also often to be found as a counter ligand to homogenous transition metal complexes research for catalysing a plethora of chemical conversions in the liquid phase: similarly however, the precise role this ligand may be playing in the desired chemistry, or indeed undesirable aspects such as catalyst deactivation, are far from well understood.

Soft X-ray XAFS potentially provides a means to investigate the speciation and structure of such elements in both ex-situ and, more importantly, *in operando* manners.

Experimental.

A previously existing vacuum apparatus and highT/lowT cryostat was used to mount powder samples, a Vortex fluorescence detector, a dosing system for volatile organo-metallics, and a gas line for the exposure of samples to H₂ and CO.

Samples were mounted within this system either using conductive carbon tape to stick the samples to an existing Cu stub, or suspended in isopropanol before being sprayed (or dropped) onto Al₂O₃ plates which were then subsequently attached to the Cu stub.

[Rh(CO)₂Cl]₂ was sublimed in situ onto γ -Al₂O₃ (Johnson Matthey) previously sprayed onto the Al₂O₃ plates. By using the variable temperature capacity provided by the cryostat these species could be studied as multilayers (100K) and then progressively as monolayers (at RT) and then in situ as they were exposed to H₂ and eventually to CO up to a temperature of ca. 613K*

Results

1. Cl containing Ir organometallics.

Figure 1 shows XANES spectra from a Cl containing Ir-Cp* catalyst immobilised on polystyrene (at 5% w/w Ir). These samples are studied in an ex-situ manner and for the as made material, the materials after three cycles as a catalyst, and as a completely “spent” catalyst.

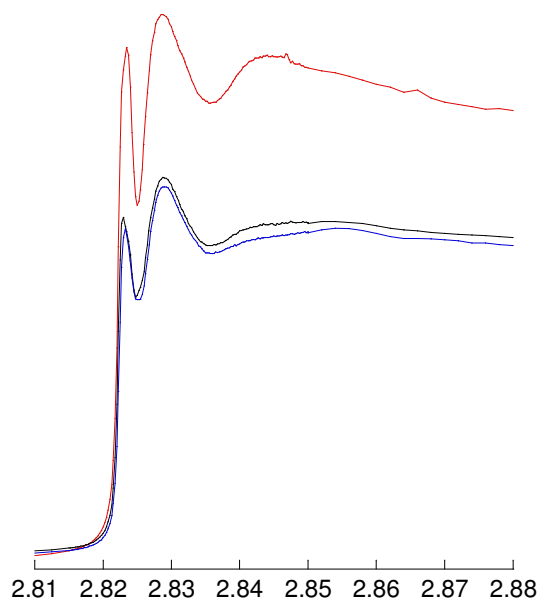


Figure 1 Cl K edge XANES derived from “fresh” (red), “3 Cycle”, and “spent” Cl-Ir catalysts.

Several alterations to the state of the catalyst from the perspective of the Cl Kedge, and as function of employment as a catalyst, can be readily detected.

Firstly, after 3 catalytic cycles, it is apparent the ca. 30% of the Cl initially present in the “fresh” catalyst has been lost. Moreover, the Cl that remains in the “3 cycle”, and eventually the “spent” catalyst, shows a significantly different XANES envelope indicative of significant structural change that has occurred as a result of the catalysis itself.

Modelling of this XANES in tandem with the more readily obtained XAFS from the Ir L3 edge will eventually lead to a far more complete description of the behaviour of this catalyst than could otherwise be obtained.

2. Cl containing Rh/Al₂O₃ catalysts

Figure 2 shows raw Cl K and Rh L3 edge XANES from a 0.5wt%Rh/Al₂O₃ catalyst and collected using 10 seconds/point during ESRF “4 bunch” operation. In these experiments the samples were measured at 298K under ca. 10⁻³ mbar H₂ (red curves). Subsequently the samples were heated to 373K (blue), 573K (green), and 613K (black) whilst continually under an H₂ atmosphere.

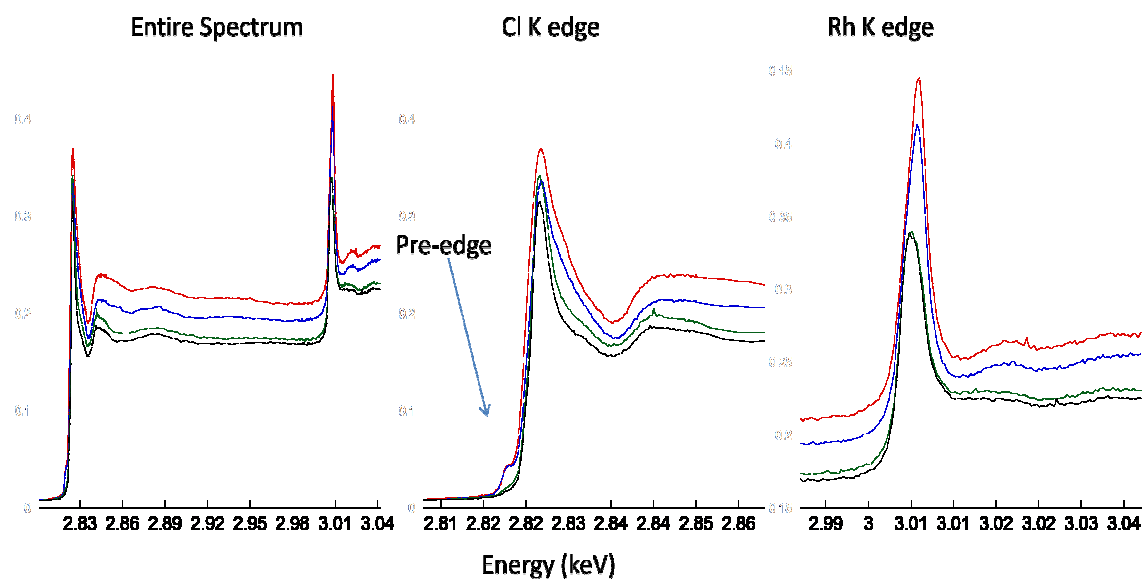


Figure 2. Cl K and Rh L3 edge spectra derived from 0.5wt%Rh/Al₂O₃ samples heated under 10⁻³ mbar H₂: 298K = red; 373K = blue; 573K = green; 613K = black.

Figure 3 shows the raw intensity ratio for a range of Rh/Al₂O₃ samples observed under H₂ and as a function of Temperature.

From simple inspection of these results a number of important aspects of the behaviour of this system may be readily obtained. Firstly that the level of Cl retention in these systems is a significant function of the Rh loading; and, secondly, that the degree to which Cl is removed during subsequent temperature programmed reduction to 613K is also very dependent on the starting Rh content.

Lastly, and though not shown here the level of Cl retention also seems to be related to the facility of reduction of the Rh phase. Importantly these results demonstrate the previous claims, based upon laboratory X-ray fluorescence measurements that have stated that no Cl is retained in very similar systems treated in very similar manner (equivalent to the 2RhA in figure 3), are clearly erroneous in this sense.

Further the Cl edge EXAFS, from these samples as well as a variety of standards show pre edge structure that appears to be indicative of Cl symmetry and bonding (and which, in figure 2, disappears with heating). It is hoped that modelling of the XANES together with DFT calculations will specify the exact nature of the information carried in this pre-edge feature and eventually be able to pinpoint the modes of Cl coordination present in these systems.

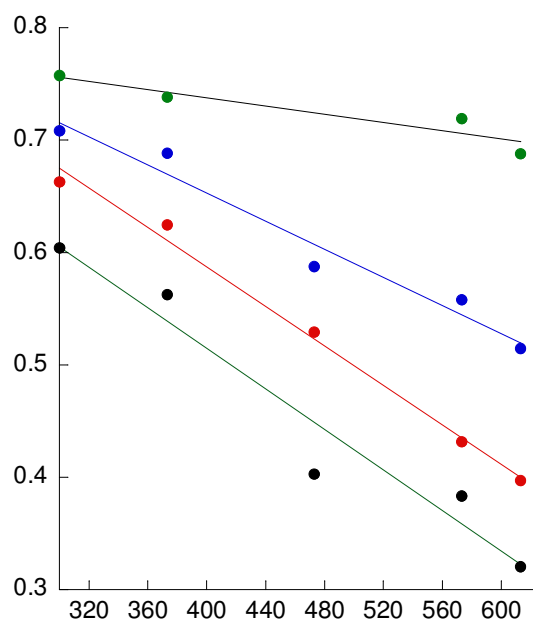


Figure 3. The Raw Cl K/Rh L_3 edge intensity ratios derived from a range of Rh catalysts, as a function temperature and under an H_2 atmosphere.

3. MOCVD of $[Rh(CO)_2Cl]_2$

In situ deposition of a volatile Rh organometallic ($[Rh(CO)_2Cl]_2$) was also undertaken. This dimeric species is of interest both as an exemplar of Cl bonding to Rh in bridging (multilayer) and linear (monolayer) geometries, but also fundamentally as a reactive surface organometallic species and catalyst precursor. For the purpose of this report an example is also give to demonstrate the capacity of BM28 to go further than XANES but also to be able to obtained EXAFS.

Figure 3 shows a spectrum derived from a multilayer of the dimeric ($[Rh(CO)_2Cl]_2$), dosed “cold” onto an Al_2O_3 powder that has previously been sprayed onto a flat Al_2O_3 plate. In this bridged $Rh^I-Cl-Rh^I$ system we can easily see that the relative intensity of the Cl K edge pre edge feature is greatly enhanced relative to that arising from the supported catalysts shown previously.

Moreover, figure 4 also shows that we can extract EXAFS from this data in so much as the proximity of the Rh L_3 edge will allow. Simple fitting of the Cl-Rh and bridging (Cl-Cl) scattering pathways expected in the dimeric system can be shown to fit the EXAFS rather well

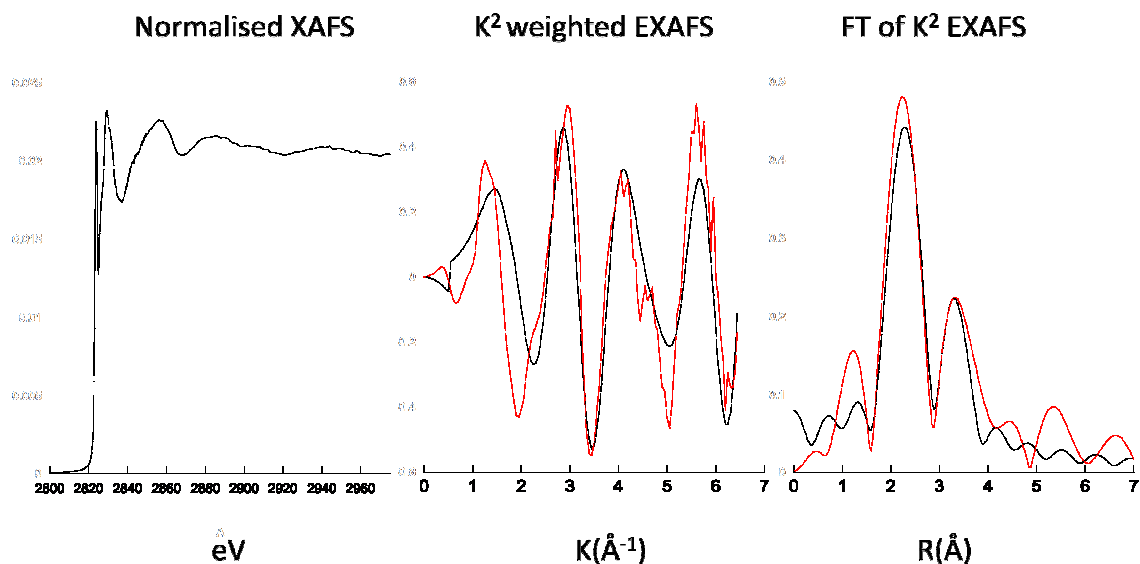


Figure 2. Raw Cl K edge XAFS from a multilayer of $[Rh(CO)_2Cl]_2$ along with the extracted EXAFS in k^2 -weighted and Fourier transform representations.

Conclusions.

We have used Cl K edge XAFS to make preliminary studies of the potential of BM28 as a resource making XANEs and EXAFS measurements in the sub 3 KeV regime. It seems clear that even with the (in some ways) non optimised measurements made here, and the use of the “4 bunch” mode of the ESRF, that XANEs and EXAFS from even relatively dilute systems can be obtained at the Cl K edge and for the L_3 edges of chemically important elements such as Rh (in principle the L_3 edge of the 4d transition metal elements from Nb upwards).

It seems clear that with foreseen beamline improvements, and optimisation of geometries, detectors, and sample environments BM28 could become a significant new resource (in a world where few currently exist) for a wide range UK and European researchers whose chemical investigations would benefit greatly from access to such a facility.