Beamline report: CH-4992

Operando DRIFTS/PDF investigation of the structure and reactivity of supported FeOx and CuOx clusters for selective conversion of methane to methanol

Main Proposer: Mark Newton
Local contacts: Sara Goberna, Stefano Checchia.

This complex experiment (involving an untried setup of DRIFTS and PDF, Figure 1) along with the requirement for handling all samples in the ESRF glove box in the central chemistry lab, and the bespoke construction of a high purity gas handling system) was, in the end, successful and all our original planned measurements were made. In addition we also were able to make some test measurements concerning other catalysts to assess the feasibility of further measurements.

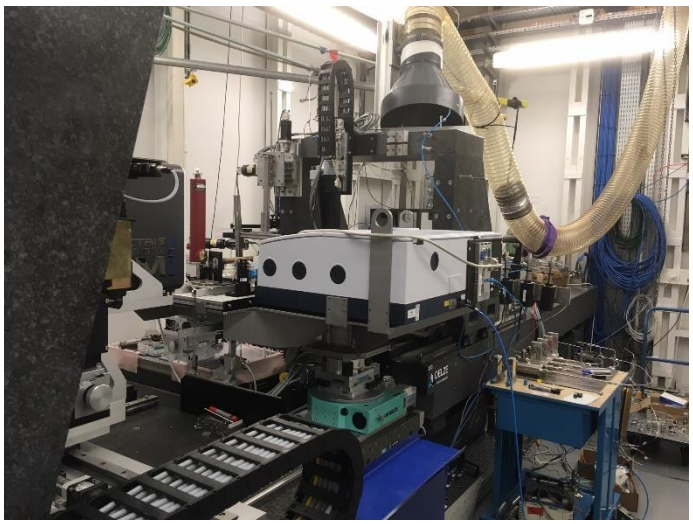

Figure 1. *DRIFTS/PDFMS setup on ID15 A and with detector withdrawn. The mass spectrometer is not visible in from this viewpoint. The entire setup was mounted and aligned (for both PDF and DRIFTS) by the users and beamline staff and bespoke gas lines constructed over the first 24hrs of the experiment.*

This was due in no small part to the communication engaged in by the local contacts with the principle proposer over a number of months in respect of the development of the IR resource on ID15A.

At the time of writing, only partially processing of the PDF data has been achieved. The early indications (provided by S. Checchia) regarding the quality of the collected PDF using the new Dectris flat panel detector data are, however, excellent. On ID15 A this method is clearly sensitive to what are subtle structural rearrangements occurring as a function of the chemistry (Figures 2 (a) and (b)). These figures aim only to demonstrate this sensitivity as a function of reactive environment attained using PDF on ID15A

In terms of the provision of the X-Rays, the refurbished ID15A must be considered as an unqualified success on the bases of these results, though only time will tell what structural details may be obtained through modelling and fitting of this data.

In addition we have validated the overall DRIFTS/PDF setup and obtained significant results from that part of the experiment on some difficult systems (e.g. Figures 3 and 4), at temperatures up to around 300 C and pressures of up to 6 bar. Some aspects of this setup (e.g. heating, accuracy of sample temperature measurement, and the use of the mass spectrometer) need to be refined and better understood; but this is always the case when putting up a complex experiment for the first time.

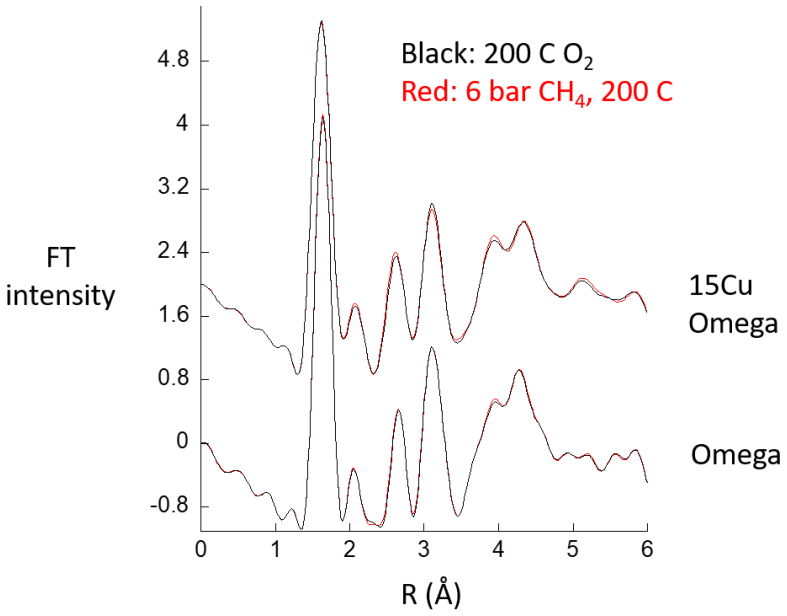

Figure 2 (a). *PDF in the 0-6 Å range for both a Cu-free (Omega) zeolite and a Cu loaded Omega at 200 C under O_2 (red) and at 200 C under 6 bar CH_4 pressure. As expected, the scattering the bulk zeolite structure dominates the patterns. However, change as a function of applied circumstance and chemistry can be detected.*
See also figure 2(b)

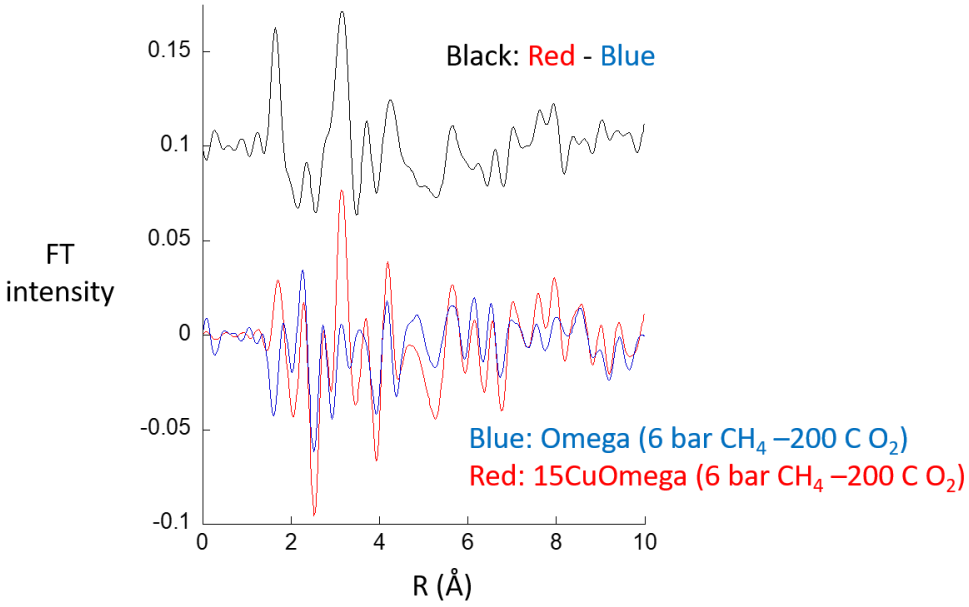

Figure 2 (b)*. Difference PDFs; Blue: difference between unloaded Omega under 6 bar of CH_4 at 200 c – under O_2 at 200 C; Red: Cu-loaded omega under 6 bar CH4 – 200 C under O_2.*
The top difference compares the Cu loaded and unloaded systems. PDF on ID15A is therefore sensitive to subtle structural change in these systems. We note that in this fist use of the setup it was not possible to properly calibrate the temperature of the sample compared to the temperature reported by the control system. As such, it seems most likely that the actual sample temperature was less than 200 C and that we were not fully accessing the complete chemistry and structural changes occurring in this system. The results however clearly show that PDF no ID15A is very sensitive to these events and can provide a new route to their definitive comprehension.

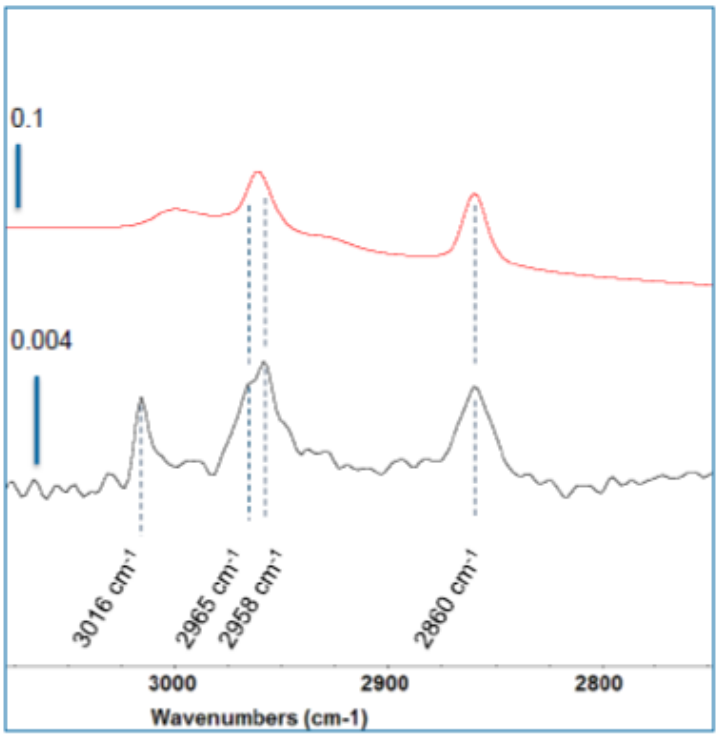

Figure 3. *Background subtracted DRIFTS collected on ID15 (bottom trace - grey) in parallel with PDF and MS. This shows the formation of adsorbed methoxy and methanol during exposure of a surface grafted (to SiO_2) Cu organometallic to CH_4 (P_{max} = 6 bar). The top trace (red) is derived from exposure of the Cu-free support materials to methanol at RT.*
Note the absorbance scale bars. Only a well-aligned and stable DRIFTS system can return such high quality and sensitive IR data.

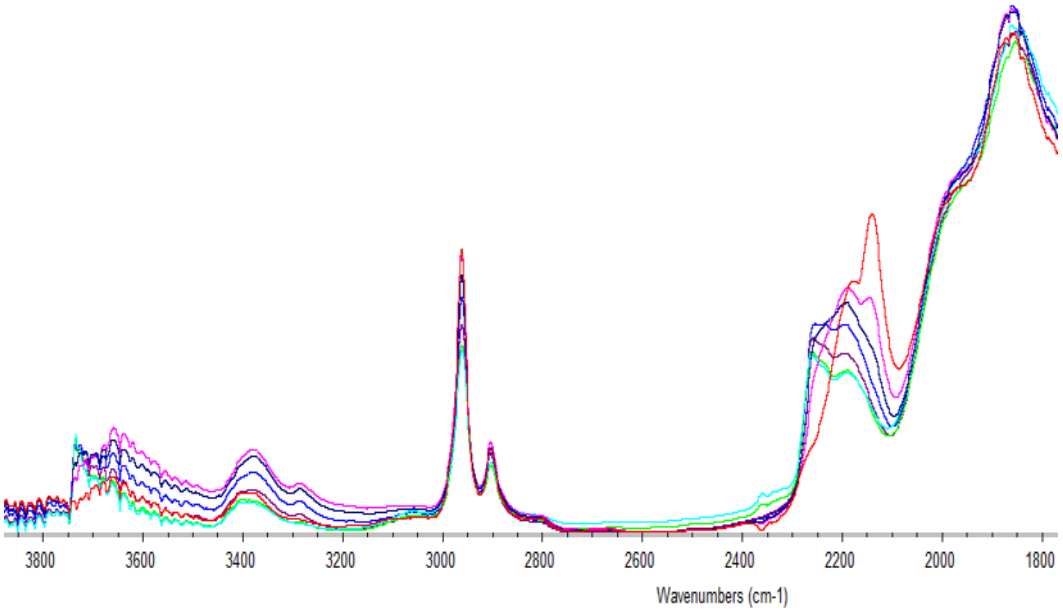

Figure 4. DRIFTS collected in parallel with PDF for a surface (SiO_2) bound Fe-hydride organometallic complex during heating under Ar to 300 C. The systematic removal of the hydride species (2131 cm^{-1}) and replacement with Si-H (2200 cm^{-1}), along with removal of species related to other ligands 2800-3000 cm-1) and changes in the degree of hydroxylation of the SiO_2 (ca. 3750 cm^{-1}) are all observable.