

**Experiment title:**

In situ energy-dispersive EXAFS studies of heterogeneous transition metal catalysts

Experiment number:

CH450

Beamline:
ID24**Date of experiment:**

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Shifts:
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Report:

The first attempt at ID24 to utilise a pulsed-flow microreactor for energy dispersive EXAFS characterisation of the structures of heterogeneous catalysts *in situ* was carried out. Quartz tubes were used for the catalyst bed and the reactor was commissioned for continuous gas flow only. Rhodium K-edge spectra were taken of materials consisting of *ca* 2 - 5 wt % of Rh on a high area titania (Degussa P25). A bent Laue-geometry Si(111) monochromator was used.

Considerable difficulty was encountered in obtaining any EXAFS data. The general concept had been previously tested on Station 9.3 of the SRS using the Pt L(III) edge to study metallisation from platinum complexes within mesoporous silicas. High quality EXAFS data could be obtained readily on 5 wt % platinum and so the difficulties on ID24 were unexpected. After substantial efforts in fault finding, it appears that the problem was mostly due to scattering from the titania particles which resulted in extremely noisy post-edge data, even for samples with a substantial edge jump.

The promise of the approach though was confirmed by experiments on $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$

supported on high area alumina. The synthesis was carried out at the beamline from toluene solution. On drying overnight on a vacuum line, the characteristic yellow colour of the $\{\text{Rh}^{\text{I}}(\text{CO})_2\}/\text{Al}_2\text{O}_3$ surface species was lost. However, exposure to CO within the tube reactor readily reformed the dicarbonyl. Two thermal decompositions were carried out in a helium flow. The first was to 500K resulting in the formation of a dark grey material with large metal particles. With a temperature ramp to 450K, a paler material was formed indicative of a higher metal dispersion. Analysis of the EDE data of these experiments is underway. Attempts were made to reform the yellow dicarbonyl on exposure to CO at room temperature, but the metal particles appear resistant to this corrosive adsorption under these conditions.