ESRF

**Experiment title:**

# ENERGY DISPERSIVE EXAFS STUDIES OF TITANIA-SUPPORTED RHODIUM CATALYSTS PREPARED BY MOCVD

**Experiment number:**
CH145

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ID24

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**Report:**

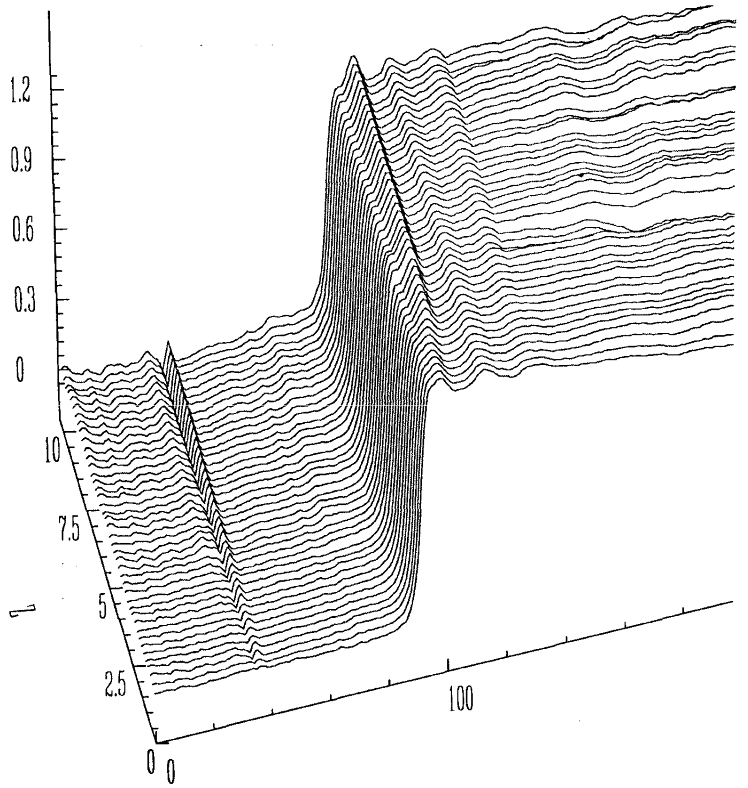
In recent years we have embarked on a large programme in which the chemistry of transition metal centres on the surfaces of oxide supports has been monitored on both a single-crystal and a powdered oxide support ($TiO_2$).[1] The former provides the fundamental information from which to interpret data on the latter. To achieve the clean conditions and uniform arrays, the metals are introduced either by metal vapour deposition or by metal-organic vapour deposition (MOCVD). We have previously demonstrated by scanning X-ray absorption spectroscopy that large fcc metal particles form after heating $Rh^{I}(CO)_2/TiO_2$ {formed from MOCVD of $[RhCl(CO)_2]_2$ onto anatase-rich powdered titania} to 400 ‘C *in vacuo.* Indications are that there are intermediate rhodium chlorides prior to the reduction. It was also known that hydrogenation also caused the reduction of these isolated Rh(I) sites, but little was known about the precise conditions underwhich the reduction took place.

Energy dispersive Rh K-edge EXAFS (EDE) experiments were performed on the thermolysis and hydrogenation of $Rh^{I}(CO)_2/TiO_2$ samples with *ca* 3 wt % rhodium *in situ* within an environmental cell. These were carried out with a bent asymmetric-cut Si(111 ) monochromator in a Laue geometry cooled by an In-Ga eutectic bath; the detector was a 512x512 element

Thomson CCD camera operating in a PDA emulation mode. The ESRF was operating in 16 bunch mode with beam currents of 70-100 mA.

EXAFS data for up to $10\text{Å}^{-1}$ could be acquired with typically 250x 15 ms scans *(ca* 6 s acquisition time). These have yet to receive detailed analysis, but the following observations are apparent from qualitative treatments on stacked plots of raw data (e.g. Figure 1).

**Figure 1:** Stack plot of Rh XAS spectra during reaction of $Rh^{I}(CO)_2/TiO_2$ with $H_2$.



When $Rh^{I}(CO)_2/TiO_2$ was heated *in vacuo* (10-5 mbar) as the sample temperature was ramped form ambient temperature to 300°C, it was apparent that there was a smooth transformation of Rh(CO)2 into metallic rhodium above 220°C, with no identifiable intermediate. Alternatively, when the sample was heated under flow of $H_2$ (1 0ml/min) within the vacuum system as the temperature was ramped, reduction with $H_2$ to metallic rhodium particles occured most rapidly with the band 80- 90°C which transpired within 1 minute. Isothermal experiments near this temperature band suggest that the reduction may be autocatalytic.

Other envisaged experiments, such as the reaction of $Rh^{I}(CO)_2/TiO_2$ with NO,[2] and the reforming of the dicarbonyl species from the reaction product could not be attempted due to equipment difficulties.

**References:**

1 J Evans, B. E. Hayden, J. F. W. Mosselmans and A. Murray, *Surf Sci.,* **1994,301,61.**
**2** K. C. Cannon, S. K. Jo and J. M. White, J. Am Chem. Sot., 1989, **111,5064.**