



Experiment title:

In situ energy dispersive EXAFS studies of heterogeneous transition element catalysts

Experiment number:

CH-526

Beamline:

ID24

Date of experiment:

from: 5 December 1998 to: 11 December 1998

Date of report:

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Shifts:

15

Local contact(s):

T Neisius

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

D G Burnaby*
UK

Department of Chemistry, University of Southampton,

J Evans*

S Fiddy*

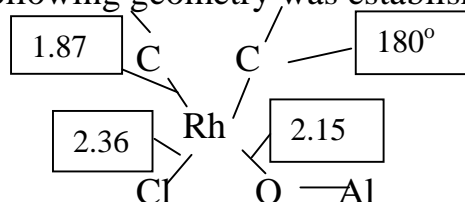
M A Newton*

A J Dent*

CLRC Daresbury Laboratory, UK

Report:

In the previous experimental run (CH450), we initiated use of a flow microreactor cell for the simultaneous monitoring of catalyst structure by EDE and the gas phase products by mass spectrometry. However, the Rh K-edge spectra of systems based on Rh(CO)₂/titania had been very disappointing, apparently due to scattering from the oxide particles. In this experiment the oxide was changed to the less dense alumina. In addition this was the first occasion on which we had benefit of the incorporation of a feedback system stabilising the beam position in both horizontal and vertical planes. These changes totally transformed the effectiveness of the experiments. Data quality was of at least comparable quality to that obtained on Station 9.3 of the SRS earlier that year.¹ Use of the Laue monochromator for the Rh K-edge EDE measurements ensured good resolution, and the flux provides very short acquisition times even through the reactor bed. For example data obtained on a bed of Rh(CO)₂/alumina (*ca* 5 wt %) averaging 100 scans with an exposure time of 1.9ms produced analysable EXAFS data to 11 Å⁻¹. Using multiple scattering analysis within EXCURV98, the following geometry was established:



Four types of experiment were carried out starting with this material:

- i) thermolysis under He (5°/minute heating rate)
- ii) thermolysis under H₂
- iii) re-exposure to CO
- iv) reaction with NO.

Thermolysis under He showed that the Rh(CO)₂ species changes to metallic particles between 180 and 200°C, with very large particles evident after heating to 400°C. Under the same heating rate, metal particle formation was evident at 57°C under H₂ and at 120°, the first coordination sphere is best fitted to 12(0.4) Rh neighbours. The next three shells in the *fcc* structure are considerably reduced in coordination number, but by 400°, further longer range ordering enhances these to close those to the values in the bulk metal. Re-exposure of CO after thermolysis under H₂ to 120°C indicated that the metal particles had not been disrupted under these conditions.

The first reaction with NO was also attempted. The Rh(CO)₂/alumina species reacts rapidly with NO to form a species with a single nitrosyl group. The reverse reaction with CO is considerably slower. The first analysable Rh EXAFS spectrum of this species was obtained. IR data show a relatively low $\nu(\text{NO})$ frequency, generally attributable to a bent nitrosyl in the surface literature, but thought to be ambiguous in the sphere of coordination chemistry. Multiple scattering treatments demonstrated that the enhancement seen for linear triatomic units was not evident, and instead a fit for a bent nitrosyl with $\angle\text{Rh-N-O}$ of 120° was apparent. A high-order multiple scattering analysis fitted a square planar complex with a coordination sphere of Rh(NO)Cl(O⁻)₂.

We wish to congratulate the beamline scientists on the highly significant improvements achieved on the beamline. Their assistance is also gratefully acknowledged for setting up the gas handling system, heating controllers and mass spectrometer.

Reference

1. S G Fiddy, M A Newton, A J Dent, G Salvini, J M Corker, S Turin, T Campbell and J Evans, *Chem Commun*, 1999, 851.