ESRF	**Experiment title:** *In situ* energy dispersive EXAFS studies of heterogeneous transition element catalysts	**Experiment number**: CH-631
Beamline: ID24	**Date of experiment**: From: 5 May 1999 to: 10 May1999	**Date of report**: 3 September, 1999
Shifts: 15	**Local contact(s)**: S Diaz Moreno	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

D G Burnaby* **Department of Chemistry, University of Southampton, UK**

J Evans

M A Newton*

S Turin*

A J Dent* **CLRC Daresbury Laboratory, UK**

Report:

Although some time was lost due to problems of focussing the Laue monochromator and some beam instabilities, the beamline generally maintained the step-function improvement achieved in December 1998. Experimental time was used to obtain a fuller picture of the chemistry of the $Rh(CO)_2$ unit on alumina. In experiment CH526, a 5 wt% sample prepared from $[RhCl(CO)_2]_2$ was heated under H_2, and this was shown to attain a Rh-Rh coordination number of *ca* 12 by 120°C. A similar temperature ramped experiment was performed using a 2 wt% sample, and this showed a lower coordination number (*ca* 10) at 140°C, showing an expected retardation of the rate of particle growth with a lower surface coverage.

Thermolyses under He and H_2 were also carried out with samples prepared form $[Rh(CO)_2(acac)]$. Again, metal formation occurs under both, but is accelerated by H_2. Under H_2, Rh-Rh bonding is evident at 90^o, with the dicarbonyl being lost by 110^0. IR data indicates that the β-diketonate is still present, but taken in conjunction with the EDE information, it is likely that this ligand has migrated to the oxide surface. Large particles

220^{o}C. Detailed analysis is underway to try to compare the changes in morphology with temperature and precursor.

The reaction of the $Rh(CO)_2$ species prepared from $[RhCl(CO)_2]_2$ with NO was investigated in detail. At room temperature the reaction is complete within 5 minutes, to form the bent nitrosyl species, $[Rh(NO)Cl(O-)_2]$ identified in CH526. After exposure to CO for 45 minutes, the dicarbonyl appears to be substantially, but incompletely reformed. At 75^{o}C, this reverse reaction is essentially complete in 1 hour. Further treatment with NO again rapidly reforms the nitrosyl species. Analysis of the gas phase indicates that these are substantially substitution reactions, with little or no NO/CO disproportionation. In these combined EDE/mass spectrometry experiments the kinetics of CO displacement by NO can be derived by MS as the structure is monitored simultaneously by EDE. In principle intensity changes in the EXAFS data should also afford kinetic information. However, some overlaid intensity periodicity is apparent, and this makes such quantitative data difficult to obtain. At higher temperatures with rapid reactions, there is closer agreement between kinetics plots obtained by MS and EDE.

Thermolysis of the nitrosyl shows testimony to its higher stability than the dicarbonyl. It is stable up to 180^{o}C, with metal particle formation becoming evident above that temperature. The rate of paticle growth with increasing temperature is also considerably reduced in the nitrosyl system, indicating that NO, or its chemisorption decomposition products, does retard particle growth. The pattern of particle growth also seems to differ form the two $Rh(CO)_2$ systems.

These experiments have shown that kinetic and structural information could be established simultanously for a clean reaction of a surface organometallic centre. Taken in conjunction with separate IR experiments, they have also begun to provide much more detailed information about the course of chemical reactions on the oxide surfaces.