



	Experiment title: Time resolved EXAFS studies of heterogeneous catalysts	Experiment number: CH863
Beamline: ID24	Date of experiment: from: 7.6.00 to 16.6.00 and 15.11.00 to 20.11.00	Date of report: 30.8.01
Shifts: 36	Local contact(s): T Neisius and S Diaz Moreno	<i>Received at ESRF:</i>
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Report:

Two aspects of this research were conducted.

The prime activity was concerned with *in situ* monitoring of the formation and reactivity of a heterogeneous catalyst, Rh/Al₂O₃ prepared from the reduction of RhCl₃ on alumina by hydrogen. A quartz capillary microreactor was employed with a mass spectrometer to allow simultaneous monitoring of the gas phase composition and the structure of the metal centres by energy dispersive EXAFS. On introduction to the reactor, the pre-reduced sample showed clear evidence of oxidation. Under mild conditions, treatment with H₂/He generates metallic rhodium, with the particle size increasing with temperature (From CN_{Rh-Rh} = ~4 at room temperature to ~8 at 300°C after ~ 15 minutes exposure to H₂/He). These particles rapidly re-oxidised on exposure to O₂/He at 100°C. From a structure showing a Rh-Rh coordination number of ~6.5, the new structure showed the following structural features: 2.7(3) Rh-O at 2.07Å; 2.6(3) Rh-Rh at 2.72Å within 15 minutes. This oxidation appears to follow two stages, with the first one occurring within 10 seconds.

Metal fragmentation on exposure to NO was even more rapid, with the disruption occurring within 5 seconds to afford a similar oxidised Rh centre, albeit with an additional Rh-N shell

(1.78Å) attributable to a nitrosyl ligand, which is observed by IR spectroscopy. Accompanied with this exothermic reaction is the evolution of N₂ and N₂O, which can only emanate from dissociative chemisorption of the NO. The temperature rise of the bed can be correlated with the known adsorption energy of NO on Rh single crystals. With the small metal particles present in these catalysts, this chemisorption is considered to form very rapid local heating of the metal particles, which fragment oxidatively under these conditions. These rapid changes in metal structure have some consequences for the understanding of oxide supported metal catalysts.

Secondly, further work on the reaction of RhCl(CO)₂/Al₂O₃ was carried out resulting in a publication, the abstract of which is presented below.

Simultaneous Determination of Structural and Kinetic Parameters Characterizing the Interconversion of Highly Dispersed Species: the interaction of NO with Rh^I(CO)₂/γ-Al₂O₃.

Newton, M.A., Burnaby, D.G., Dent, A.J., Diaz-Moreno, S., Evans, J., Fiddy, S.G., Neisius, T., Pascarelli, S., and Turin, S. *J Phys Chem A*, 2001, 105, 5965 – 5970.

Energy-dispersive EXAFS (EDE), combined with mass spectrometry and a flow microreactor system, has been used to investigate the reaction of an Al₂O₃-supported Rh^I(CO)₂ species with NO. This combined in situ approach uniquely permits a priori analysis of the structures of the species involved (on a time scale of Ca. 2 s) and simultaneous determination of reaction mechanism and kinetic parameters. In the current case, it is found that the Al(O)Rh^I(CO)₂Cl species reacts to form an intermediate Al(O)Rh(NO)₂Cl species ($v \sim 0.357 \pm 0.125 \text{ s}^{-1}$, $E_{\text{act}} \sim 11 \pm 1.25 \text{ kJ mol}^{-1}$), which subsequently forms an (AlO)₂Rh(NO)Cl species and N₂O_(g) ($v \sim 2 \pm 0.5 \times 10^4 \text{ s}^{-1}$, $E_{\text{act}} \sim 40 \pm 3.5 \text{ kJ mol}^{-1}$) showing a bent (134°) RhNO bond. This combination of rapid and complementary techniques should be applicable to a wide range of disciplines where quantitative structural and kinetic determinations are of importance.