



	Experiment title: Effect of ceria on the structure and performance of nanoparticulate rhodium catalysts for CO and NO removal	Experiment number: CH2194
Beamline: ID24	Date of experiment: from: 20 July 2006 to: 26 July 2006	Date of report: 21 February 2007
Shifts: 18	Local contact(s): Dr Mark Newton	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): John Evans ^{1,2*} , Andrew Dent, ^{2*} Anna Kroner, ^{1,3*} Mark Newton, ^{3*} Andrea Russell, ¹ Moniek Tromp ^{1*} ¹ School of Chemistry, University of Southampton, Southampton, UK ² Diamond Light Source, Oxfordshire, UK ³ ESRF, Grenoble, France		

Report:

The ESRF equipment for carrying out synchronous energy dispersive EXAFS (EDE) and diffuse reflectance Fourier transform IR spectroscopy was successfully tested and applied for the study of alumina supported rhodium catalysts. This instrumentation is a development from that previously reported.¹ Samples based upon 5 and 2 wt% Rh were studied, with a repetition rate of ~ 100 ms for the IR and X-ray absorption spectra. All samples were pretreated with a H₂-O₂-H₂ cycle at 573 K prior to further study. Such materials catalyse the oxidation of CO,² and the steps in this process were monitored by pulsing between CO and O₂. The 5 wt% Rh/Al₂O₃ was held at 573 K under He and then subject to three alternate exposures of 20 s duration each of 5 % O₂/He and 5% CO/He. After returning the gas flow to He, the Rh K-edge XAFS was found to be identical to that observed initially. However, this was not due to an invariant catalyst structure, but to one that responded rapidly to the ambient gas at this temperature. The degree of oxidation varied with the gas changes, with oxidation ensuing on addition of O₂ and re-reduction by CO. This reduction was accompanied by the formation of CO₂ and further CO adopted atop sites on the metallic rhodium. Switching then to O₂/He caused the loss of the adsorbed CO, generation of CO₂ and oxidation of the metal to an oxidic phase. The degree of oxidation may be tracked by monitoring the change in height of a XANES feature indicative of the degree of oxidation of the rhodium³ (Figure 1). At 473 K, the response is slower. Also at lower temperatures, there is a higher proportion of the rhodium which adopts mononuclear Rh(CO)₂ sites after exposure of CO to the oxidic phase (Figure 2).

The effect of adding ceria to the catalysts varied with the mode of introduction. The effect of a thin surface coverage prior to rhodium deposition was relatively small. More significant changes were effected by the addition of a cerium metallorganic onto Rh/Al₂O₃. In this case some protection of rhodium from oxidation was apparent.

XANES for 5% Rh/Al₂O₃ 473 and 573 K

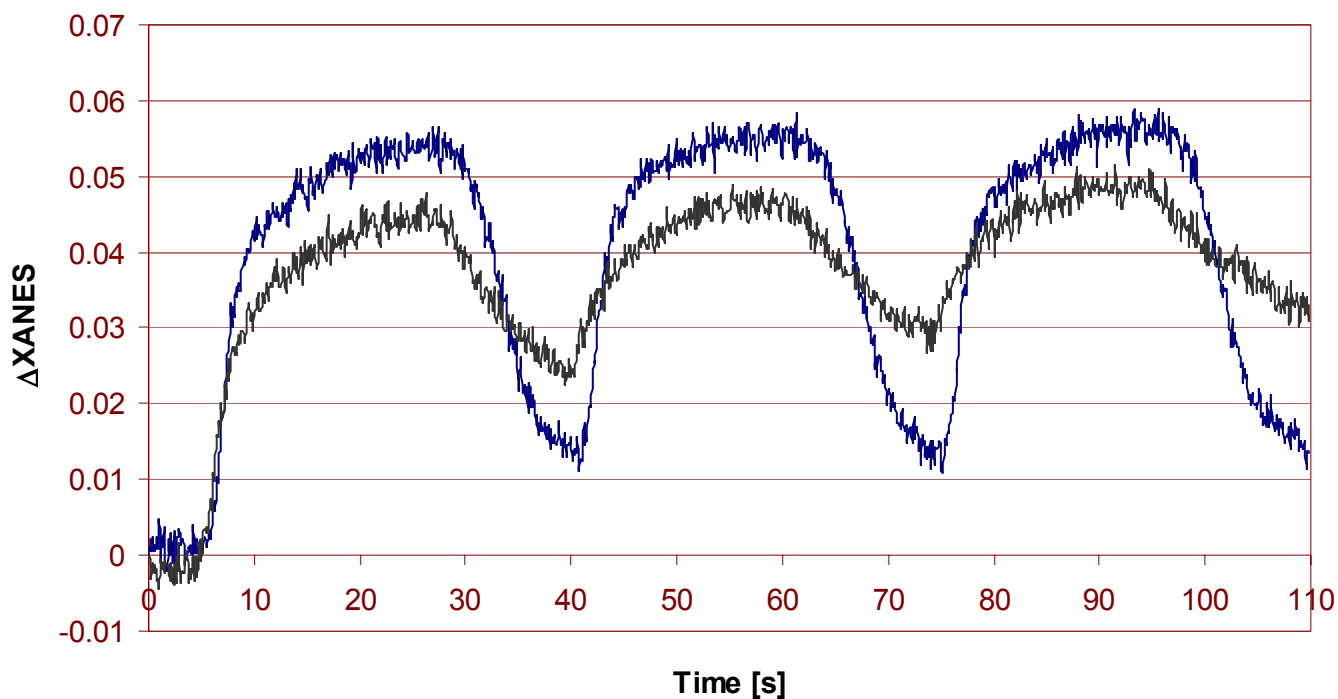


Figure 1. Variation in normalised Rh K-edge XANES at 23250 eV of 5 wt% Rh/Al₂O₃ at 573 K (blue) and 473 K (black)

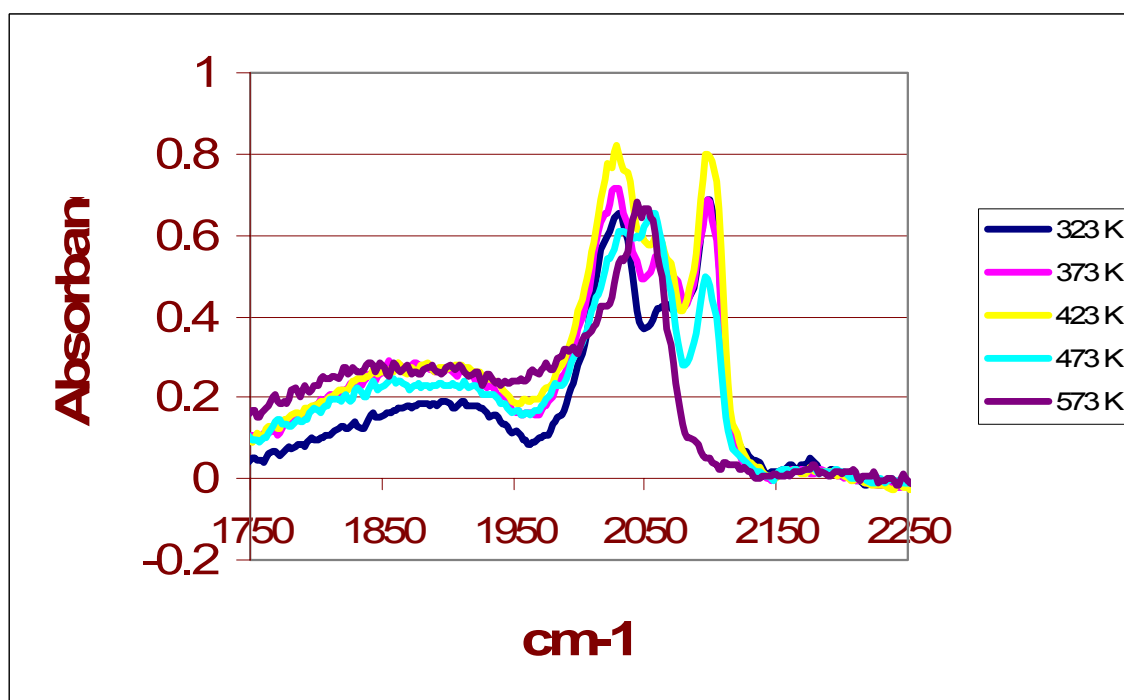


Figure 2. Variation in normalised IR spectra in the $\nu(\text{CO})$ region of 5 wt% Rh/Al₂O₃ at temperatures between 323 K and 573 K.

References

1. M.A. Newton, B. Jyoti, A.J. Dent, S.G. Fiddy and J. Evans, *Chem. Commun.*, 2004, 2382-2383.
2. M.A. Newton, A.J. Dent, S. Diaz-Moreno, S.G. Fiddy, B. Jyoti and J. Evans, *Chem. Eur. J.*, 2006, **12**, 1975-1985.
3. M.A. Newton, A.J. Dent, S.G. Fiddy, B. Jyoti, and J. Evans, *Phys.Chem. Chem. Phys.*, 2007, **9**, 246 – 249, and references therein.