	Experiment title: In situ investigations of catalyst structure and reactivity by combining energy dispersive EXAFS with diffuse reflectance IR spectroscopy	**Experiment number**: CH1370
Beamline: ID24	**Date of experiment**: from: July 2003 to: May 2005	**Date of report**: November 2005
Shifts: 116	**Local contact(s)**: S Diaz-Moreno, S G Fiddy, G Guilera, M A Newton	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

John Evans* & Mark A Newton[1],* School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

Andrew J Dent[2],* CLRC Daresbury Laboratory, Warrington, WA4 4AD, UK

Present addresses:
[1] ESRF, [2] Diamond Light Source, Chilton, OX11 0DE, UK

Abstract

A methodology has been developed to allow simultaneous monitoring of the vibrational spectra of surface adsorbates and the X-ray absorption spectra of the elements of metallic particles in operating heterogeneous catalysts. For a sample such as 5wtRh/Al_2O_3, a repetition rate of 50ms is viable both both techinques. By using multiple ion monitoring for rapid gas composition analysis, the structural changes can be correlated with catalytic performance. For example, in a gas stream of CO/NO in He, there is rapid oxidation of the rhodium to $Rh^I(CO)_2/Al_2O_3$, but it is only under higher temperature conditions in which this species begins to decompose to clustered rhodium that the reduction of NO proceed.

Report:

Introduction

This Long Term Project (LTP) was our second dedicated to developing methodologies for the application of Energy Dispersive EXAFS (EDE) for in situ structure-function studies of heterogeneous catalysts. The first of these (CH863: 2000-2001) targeted a flow microreactor cell on ID24,[1-4] and some improvements on and application of that cell were carried out during this LTP. In addition, an expansion of the spectroscopic characterisation was envisaged using Diffuse Reflectance Infra red Fourier Transform Spectroscopy (DRIFTS). Speciation of surface adsorbates by their vibrational characteristics could then be monitored simultaneously with the use of XAFS to probe the metal particles of the heterogeneous catalysts and mass spectrometry to track the gas phase composition after the catalysis bed. The applications have been centred upon model catalysts for the three-way automotive exhaust catalyst, with Rh/Al_2O_3 as the core heterogeneous catalyst.

Experimental developments

In the application for CH1370, three milestones were proposed:

i) *Construction of the DRIFTS/EDE/MS cell*

The DRIFTS-XAFS cell was based upon a commercial (Spectratech) optical system with a modified reactor cell. The sample, as a powder, is contained within a boron nitride tubular cup heated from below. The reactor cell has two BN windows for transmission XAFS and a CaF_2 IR window on top. The outline of the experimental system is presented in Figure 1. The IR spectrometer has a rapid scanning capability (up to 80 spectra/s at low resolution), and to achieve this with great reliability requires a substantial optical bench upon which to mount the interferrometer. This instrumentation is maintained at the University of Southampton for catalyst studies and was transported to the ESRF for the experiments reported herein.

If the internal diameter of the sample cup is in the 3 -5 mm range, then the FT-IR spectrometer can provide satisfactory IR intensities in ~50ms for M-CO and M-NO bands from dilute catalyst samples (> 1wt%).

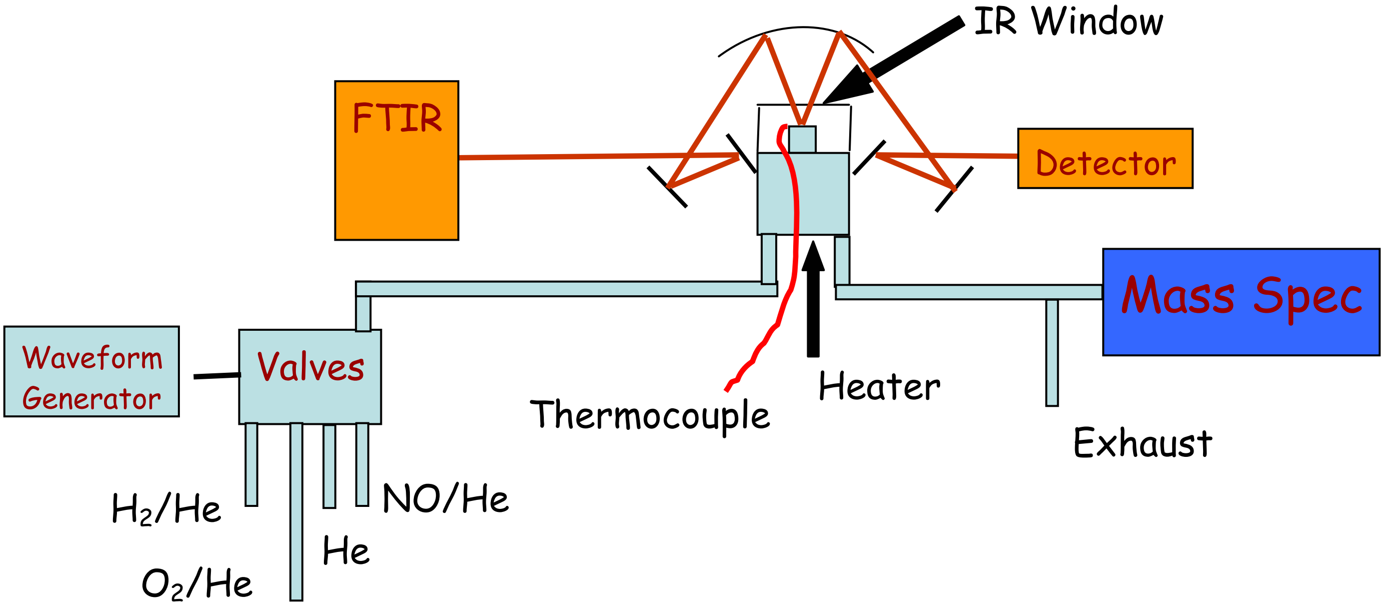

Figure 1: *Schematic layout of DRIFTS/XAFS/MS sampling system.*

ii) *Commissioning of EDE/DRIFTS/MS on ID24*

The sampling system presented in Figure 1 is mounted on an external optical bench as shown in Figure 2

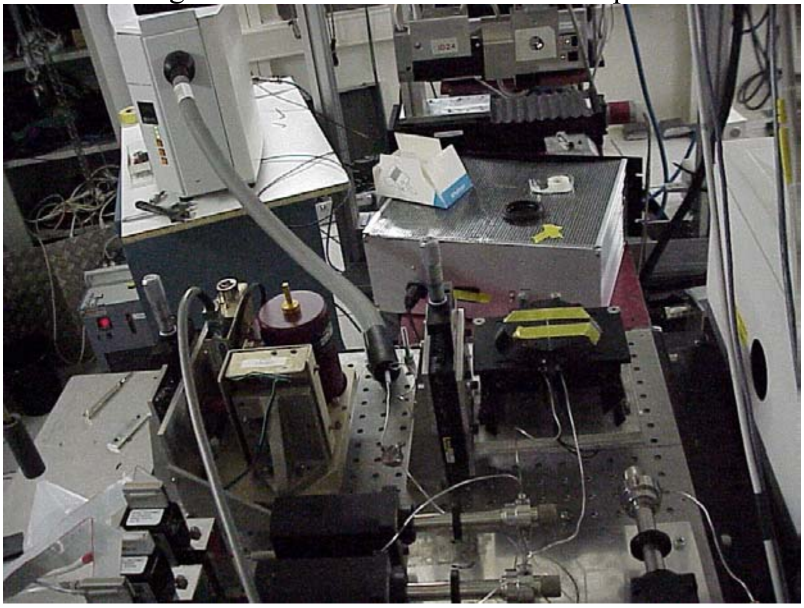

Figure 2: *Viewed along the 2θ arm of ID24 towards the EDE detector. The DRIFTS cell is seen between the IR spectrometer and the IR detector. The capillary sampling lead to the mass spectrometer is also shown.*

(photographed on ID24). Due to the requirement of EDE to move the sample out of the X-ray beam in order to record an independent I_0 spectrum, the IR spectrometer and external bench were mounted on a translation table. In practice acceptable IR and XAFS data could be recorded with a ~50ms acquisition time. However this was only achieved in 2004 and 2005 after a series of significant improvements in the capability at ID24.

These were:

a) Optical components

The beam line staff carried out a substantial quality improvement programme in 2004 which reduced the structure of the background spectra caused by imaging of imperfections on mirrors, windows and monochromators. This contributed to a step change in data quality in July 2004.

Two alternative monchromators have been utilised. Until July 2004, the transmission (Laue) geometry was employed to avoid the broad reflectivity properties of a Bragg Si(111) monochromator at > 20keV, substantially due to penetration into the crystal. However, a higher order Si(311) Bragg monochromator was found to restore the effective spectral resolution and provided a stable optical system. This was a highly satifactory arrangement for most of the experiments performed, but is not appropriate for very small sample cells (due to the increased focal spot) or for some twin edge experiments (due to the narrower energy spread).

b) Global feedback system

This beam line upgrade coincided with the institution of gobal feedback of the horizontal orbit of the ring; this too may have contributed to the improvement in data quality (Manifested in increased apparent S/N and valid *k* range).

c) Detector developments

The restriction of the read-out time (~0.3s) imposed by the Princeton CCD detector has been a significant limitation in all time resolved studies. In principle, for a restricted number of spectra (initially ~14) this could be circumvented by measuring spectra in a single stripe mode. However, this is also very inconvenient since the only effective way of modifying the time span of the experiment is to change the exposure time by adding or removing filters in the X-ray beam. Tests in July 2004 showed that use of the FReLoN camera in a single stripe mode could provide a potential repetition rate of ~1ms, and so this was no longer a limitation to the experiment. Unfortunately the detector proved to be unreliable in a later run in December 2004. However, work carried out in 2005 on a new FReLoN camera and data acquisition system seems to make this the current detector of choice for time resolved measurements in the ms – s timescale.

For those elements with high energy X-ray absorption edges (*e.g.* Rh and Pd K-edges) sufficient transmission through the favoured DRIFTS sample cup diameter was attainable to give a good time resolution match between the IR and XAFS measurements. However, at softer edges (*eg.* Pt L_{III}) the lower X-ray attenution length removes this compatability and a new sampling arrangement will be required for studies of *3d* and *5d* elements.

iii) *Establish gas flow modulation synchronised with data acquisition*

As shown in Figure 1, a waveform generator can be employed to modulate gas flows. It is important to be able to change the gas compositions rapidly to avoid the restriction of only monitoring steady state species. Whilst that is important in studying catalytic porcesses, considerably more insight is afforded if the structure and kinetic behaviour of transients can be monitored. The requirement of the Princeton CCD camera to be the master in all synchronisations was a major drawback in setting up pulsed and modulated experimental trains. However, the FReLoN camera is able to respond to external triggers and thus forms a highly viable platform for time resolved experimentation.

When all these experimental parameters are optimised, then the data flow from three techniques operating at about 20 spectra per second is very high. So it has become apparent that a more automated process of data logging and reduction is necessary to ensure the density of data acquisition to be turned into a depth of scientific understanding in a finite time. This we are currently tackling from the standpoint of a high throughput XAFS system.

Catalytic chemistry

The fourth milestone was the *Characterisation of three-way exhaust gas catalysts* using the new instrumentation.

With the previously established microreactor cell[1,5] new information about the structural response of Rh/Al_2O_3 to ambient conditions could be established. These have included the effect of sulfur-containing poisons,[6] and the kinetics of the Rh/Rh_2O_3 couple.[9]

Detailed catalytic experiments have also been carried out, particularly on CO oxidation[11] and NO reduction (by H_2).[7] In contrast to the case of NO reduction,[4] both the oxidised and metallic phases of Rh/Al_2O_3 catalyse CO oxidation; in further contrast, oxidation of rhodium does not suppress catalytic activity but enhances it. Under NO/H_2, the deleterious oxidation of rhodium by NO can be suppressed by alloying with palladium.[7] The alloying also reduces the temperature required for the onset of catalysis. Unfortunately the preferred selectivity of this reaction to afford the environmentally benign N_2 is significantly reduced as more N_2O is generated.

Interestingly too, under high CO/O_2 ratios, there was strong evidence for the co-existence of $Rh^I(CO)_2/Al_2O_3$, albeit as a spectator species.[11] The rate of corrosive chemisorption of CO alone is strongly dependent upon the metal particle size. At a 5wt% loading, after 36 s the majority of Rh is within metallic particles, with CO sites evident on both metallic and some $Rh^I(CO)_2$ centres.[12] However, after the same time interval, for the more dilute 2wt % samples, which consists mainly of small clusters, the XAFS pattern changed to that akin to that of $Rh(CO)_2$. The IR studies showed that the adsorption of CO was complete in about 10s at room temperature (**Figure 3**).

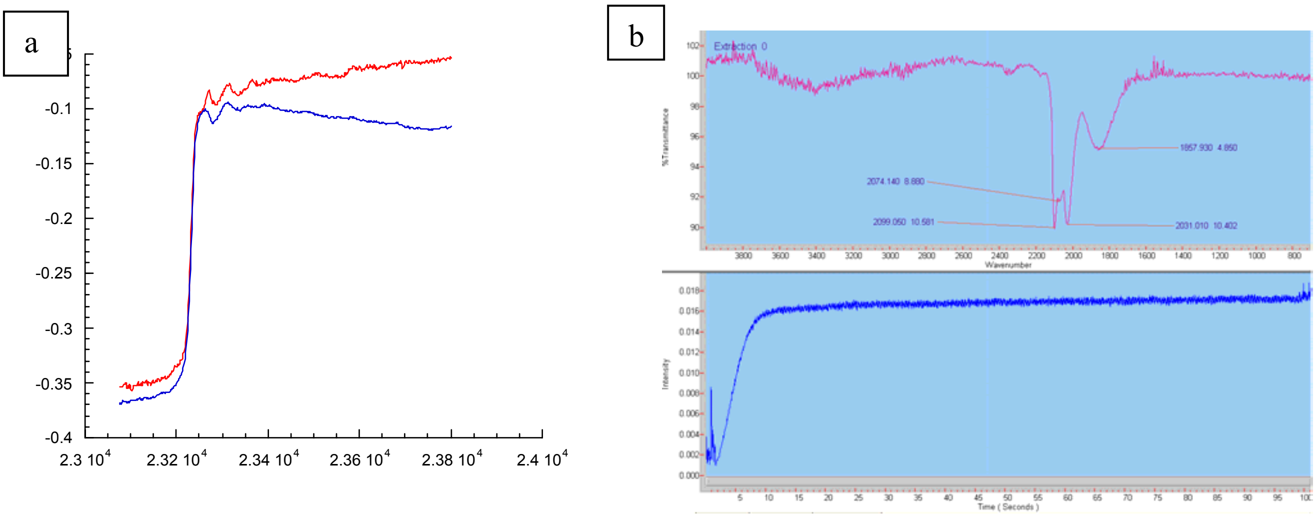

Figure 3: ***a)*** *Rh K-edge XAFS of 2wt%*Rh/Al_2O_3 *before (red) and after (blue) CO exposure for 36s. b) Lower: change in IR absorption with time after CO exposure; upper – DRIFTS spectrum covering ν(CO) and ν(OH).*

In the other main reaction for removal of CO and NO from exhaust streams, *viz.* their direct reaction to CO_2 and N_2 (and/or N_2O), it was observed that these gases in combination are more corrosive to metallic particles containing rhodium than either by itself. So, as shown in Figure 4, formation of $Rh(CO)_2$ units is the dominant event on exposure to NO/CO at room temperature.[12] The metal is mainly sequestered as that species to a temperature of ~450K, when its conversion to metal clusters ensues. It is at this temperature also that the reduction of NO by CO starts to take effect.[8]

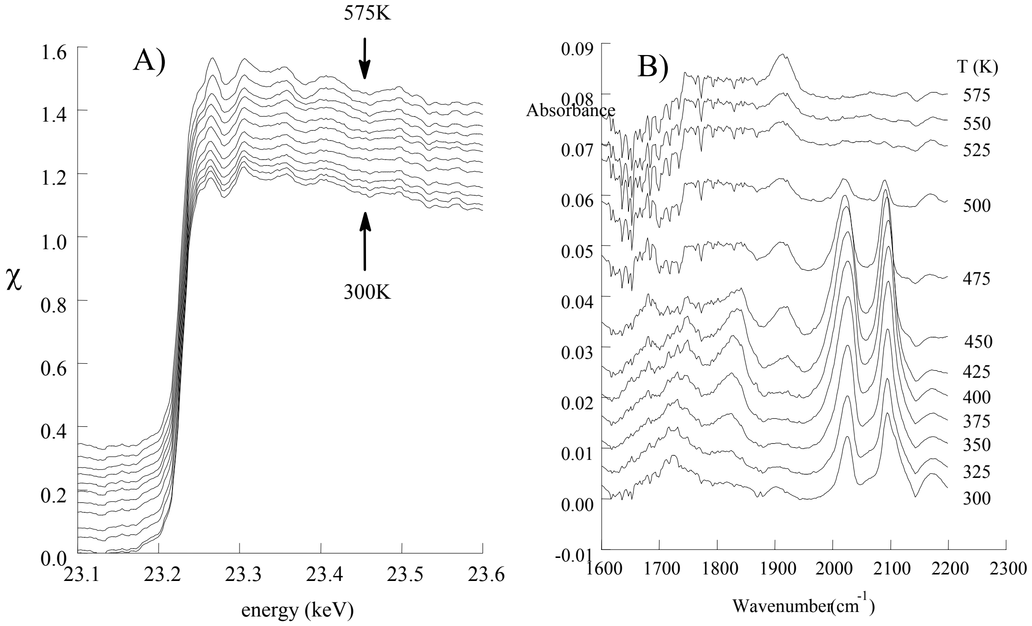

Figure 4: *Spectra of 5wt% Rh/Al_2O_3 under 2.5%CO+2.5%NO/He at increasing temperatures. A) Rh K-edges XAFS. B) DRIFTS spectra.*

Conclusions

The sampling system for combined transmission XAFS and Diffuse Reflectance Infra red Fourier Transform Spectroscopy has been developed and untilised on Beam line ID24 to provide considerable insight into the chemistry of heterogeneous catalysts. This prototype offers time resolution of 50ms for these two techniques when investigating the K-edge of *4d* elements. Other cells will be required for softer edges. Nevertheless, this LTP provided the basis upon which to establish combined XAFS-IR with sub-second repetition rates at that beamline. Indeed similar instrumentation is being constructed at the ESRF to offer this provison to other user groups.

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