

## High throughput *in situ* EXAFS instrumentation for the automatic characterization of materials and catalysts.

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### Introduction

The development of intelligent and modular instrumentation is imperative for the identification of catalysts and materials with new functionalities. Integration of many analytical techniques under a single high throughput (HT) experiment enables detailed screening of numerous candidates and reduces experimental time [1]. Parallel experimentation increases the probability of significant discoveries by revealing interesting trends, promoting efficient use of available resources and allowing reductions in research costs. In catalysis and materials research, EXAFS is used routinely for characterisation of the electronic and local geometric structure during catalytic reactions [2,3]. In contrast to the expanding use of HT XRD [4], the inherent advantages of EXAFS have not been realised in HT research and represent unharvested potentials [5].

### Methods and Materials

A HT XAFS data acquisition and control system for the *in situ* analysis of dynamic materials libraries under control of the temperature and gaseous environments has been developed. The system comprises of a XYZθ-positioning stage that allows precise positioning of highly compact arrays (> 1M discrete materials/cm<sup>2</sup>). Multiple mass flow control and quadrupole mass spectrometry allowed concurrent determination of catalytic performance of libraries of various sizes. The system was initially tested (without mass spectrometric measurements) using a library of 91 candidates consisting of ternary Al<sub>2</sub>O<sub>3</sub> supported powder catalyst precursors containing Cu, Pt, and Au. An SBS standard, 96 well-plate has been adopted for the synthesis of library members with different metal concentrations, which also enables compatibility with common synthesis robots. EXAFS spectra were obtained at the Cu K, Pt L<sub>III</sub> and Au L<sub>III</sub> -edges, at station 9.3 of the Synchrotron Radiation Source (SRS) at CCLRC Daresbury Laboratory, UK. Additionally, a custom made 8-fold microreactor was used that permitted additional investigations while monitoring catalytic reaction rates with by MS. The catalysts investigated in this system contained different concentrations of Au on Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> supports. Automated data reduction software was developed based on the IFEFFIT [6] library. It was also used for performing an automated standard EXAFS analysis, generating matrices of structural and electronic parameters.

### Results and Discussion

Fig 1(a) demonstrates the connectivity between the different components of the high throughput setup and the synchrotron station. Various protocols, including the industry-standard Profibus were incorporated for flexibility and expandability. Temperature programmed reduction of a catalyst in the 8 well reactor can be seen on Fig 1(b). Supported Au<sup>3+</sup> was reduced in an (1/1) CO/He stream, as indicated by a decrease of the near-edge feature at 11925 eV.

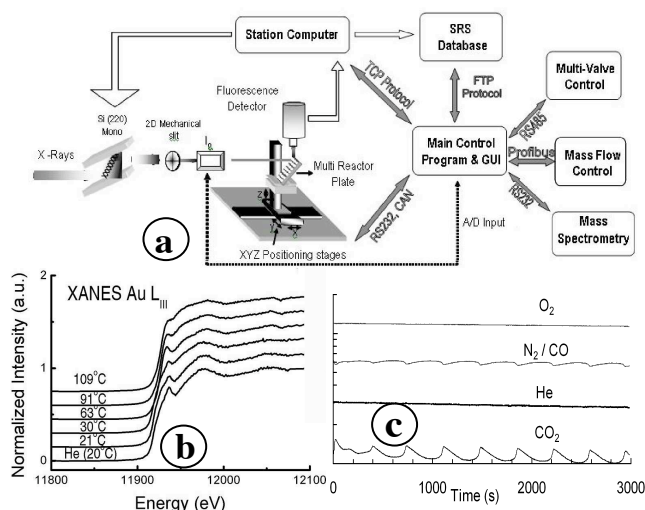


Fig.1 (a) Integration of high throughput instrumentation in Daresbury SRS Station 9.3, (b) TPR of 1% Au/Al<sub>2</sub>O<sub>3</sub> on CO stream, (c) Oscillatory behaviour of CO/CO<sub>2</sub> conversion of a 1% Au/Al<sub>2</sub>O<sub>3</sub> catalyst.

Fig 1(c) shows MS transients of O<sub>2</sub>, CO, He and CO<sub>2</sub> during CO oxidation over a 1% Au/Al<sub>2</sub>O<sub>3</sub> catalyst. After a period of 6 h oscillations in the CO/CO<sub>2</sub> conversion were observed. The frequency of these effects increased with time on stream. Rate oscillations were also present for a 4% Au/Al<sub>2</sub>O<sub>3</sub> catalyst.

**In summary**, integration of the HT system in the synchrotron station facilitated the rapid acquisition of *ex situ* and *in situ* XAS data with parallel MS, gas-flow and temperature control. Parallel control of the reduction process of the catalysts was successful. Previously unknown rate oscillations were discovered for some catalysts. These are caused by the slow development of what we believe is thermal feedback mechanism [7]. To clarify their origin the catalysts exhibiting this phenomenon will be further analysed during each cycle with faster EXAFS acquisition. The results demonstrate the potential of HT experimentation for *in situ* EXAFS studies.

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