

High Throughput *In Situ* XAFS Screening of Catalysts

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Abstract. We outline and demonstrate the feasibility of high-throughput (HT) *in situ* XAFS for synchrotron radiation studies. An XAS data acquisition and control system for the analysis of dynamic materials libraries under control of temperature and gaseous environments has been developed. The system is compatible with the 96-well industry standard and coupled to multi-stream quadrupole mass spectrometry (QMS) analysis of reactor effluents. An automated analytical workflow generates data quickly compared to traditional individual spectrum acquisition and analyses them in quasi-real time using an HT data analysis tool based on IFFEFIT. The system was used for the automated characterization of a library of 91 catalyst precursors containing ternary combinations of Cu, Pt, and Au on γ -Al₂O₃, and for the *in situ* characterization of Au catalysts supported on Al₂O₃ and TiO₂.

Keywords: High throughput, XAS, XANES, EXAFS, catalysis.

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INTRODUCTION

The development of intelligent and modular instrumentation is imperative for the identification of catalysts and materials with new target functionalities. Integration of many analytical techniques under a single high throughput (HT) experiment enables detailed screening of numerous candidates and reduces the time scale of the experiments [1]. Parallel experimentation increases the probability of significant discoveries by revealing trends in complex data sets. It increases efficiency and allows for significant reduction of research costs. HT methods have recently become more accepted in the catalytic community, with combinatorial experimentation a promising research avenue for the discovery of new catalysts and optimization of their yield and selectivity [2-4]. Besides measurements of reaction kinetics, spectroscopic methods such as infrared spectroscopy [5], Raman spectroscopy [6], X-ray fluorescence [7], fluorescence microscopy [8], imaging polarimetry [9], nuclear magnetic resonance spectroscopy [10] and X-ray diffraction [11] have been incorporated in high-throughput instrumentation. These techniques are valuable for characterizing large sample libraries but have limitations, e.g. difficulties with *in situ*

realization (nuclear magnetic resonance) or the restriction to crystalline materials (X-ray diffraction). The flexibility and inherent advantages of X-ray absorption spectroscopy (XAS) for non-crystalline systems have not been utilized in HT research and present new and promising research ground [13].

EXPERIMENTAL

The HT XAS data acquisition and control system comprises a high-precision positioning stage (x,y,z,θ) that allows positioning of highly compact arrays (more than 1000 discrete materials/cm²). For the *in situ* experiments a custom-made 8-fold microreactor array was used. Individual gas flows are supplied *via* independent mass flow controllers (MFCs); the effluent of each cell is monitored by quadrupole mass spectrometry (QMS), Fig. 1.

XAS experiments were carried out at station 9.3 of the SRS in Daresbury, UK [15]. The HT EXAFS analysis was performed using Linux shell scripts that, sequentially, (i) read all the spectra produced, (ii) applied the IFFEFIT background subtraction routine and (iii) performed a single-shell fitting analysis assuming the presence of metal chlorides. Theoretical

amplitudes and phase functions used in the fitting procedure were calculated with FEFF6 [16]. All the fits were performed using multiple k-weightings of 1, 2 and 3. The fitting algorithm required the input of initial guess values for backscattering species, edge-position, coordination number (N) nearest neighbor distance (R) and Debye-Waller factor (σ^2). The script then reports back with the shift on the edge position, the edge-step (ES) values, the normalized data, the $\chi(k)$ data, the Fourier transformed data, the fitted EXAFS curves and the resulting fitted values for N , R and σ^2 . This software performed single-shell EXAFS analysis on 96 samples at two different edges (*i.e.*, a total of 192 spectra) in approximately 15 minutes.

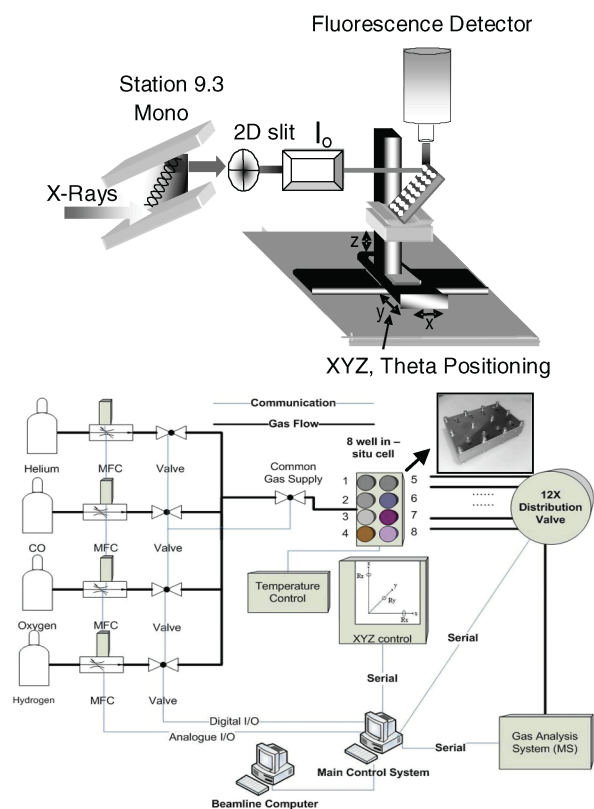


FIGURE 1. HT XAFS instrumentation in Station 9.3 of SRS Daresbury. Top: Placement of robotic stage with respect to detector and X-ray beam. Bottom: Main system components and communication interface with beamline. The inset shows the custom made 8x reactor.

Experiments with the 96-wellplate were conducted using catalyst precursors prepared by wet impregnation of a γ - Al_2O_3 (D1011, BASF) support (200-450 μm particle size) with solutions of CuCl_2 (Aldrich, 99.995%), PtCl_2 (Aldrich, 98%) and HAuCl_4 (Riedel-de Haën, 51% Au) in concentrated HCl. A standard glass 96 well plate was used to prepare and store the samples. The library comprises of permutations of Cu, Pt and Au in concentrations of 0,

0.1, 1 and 5 wt% resulting in a library of 91 elements. Figure 2a shows the Cu concentration in wt % for each of the library members. CO oxidation *in situ* experiments utilized catalysts of different concentrations of Au/TiO_2 and $\text{Au/Al}_2\text{O}_3$ and were prepared by a modified incipient method as described in [14].

RESULTS & DISCUSSION

Some of the results from the *ex situ* HT-XAS analysis of spectra taken at the Cu K-edge are shown in Figs. 2. It presents the Cu concentration in the catalysts (Fig. 2a) and the determined number N of coordinating Cl atoms (Fig. 2b). Black color in the figures indicates either the absence of the metal under study or spectra not analysed because of an extremely low S/N ratio. The usefulness of these visual maps shall be illustrated using an example. The N map (Fig. 2b) has an 'island' of samples (E6, F6 and G6) with very low Cl-coordination numbers, which are clearly non-sensical. The EXAFS from these samples were thus further examined individually.

The analysis, somewhat unexpectedly, revealed the presence of Cu metal in these samples. The plausibility of this result is underlined by the data presented in Figure 2c, which shows the full XANES spectra of samples A7 and E8 (corresponding essentially to unreacted CuCl_2), of samples E6, F6, G6 (containing Cu metal), and of Cu foil.

X-ray induced reduction of Cu^{2+} was excluded as it was not observed in any of the other samples. It was noticed, however, that the reduction to Cu^0 was limited to samples in which PtCl_2 was present. The formation of Cu^0 thus appeared to be related to the redox couple

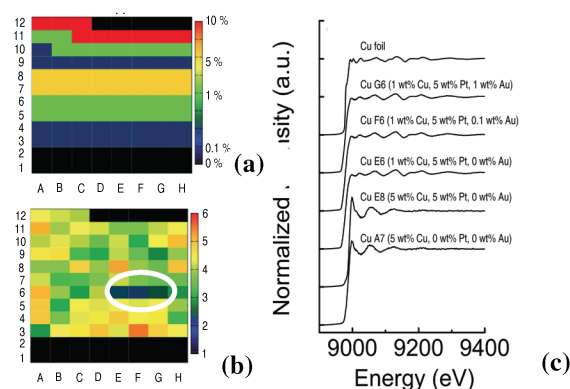
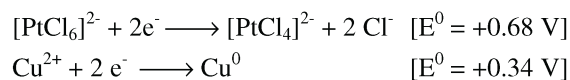
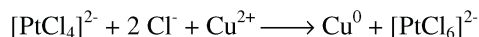


FIGURE 2. Color map representations of copper concentrations (a) and Cl coordination numbers (b) for each catalyst precursor, calculated using the script based HT analysis. (c) presents the Cu K-edge XANES spectra of precursors A7, E8, E6, F6 and G6, and of a Cu metal foil.



A more quantitative evaluation using the Nernst equation reveals that the reaction



becomes feasible at room temperature in the presence of excess Cl^- (note that we used solutions in conc. HCl) and especially during the drying process, which raises the concentrations of all reactants and thus shifts the equilibrium towards the products Cu metal and $[\text{PtCl}_6]^{2-}$. The expected oxidation of Pt^{II} to Pt^{IV} was clearly evident also through an increase of the white line in the Pt L_3 -edge XANES from these samples (an example is shown in Fig. 3).

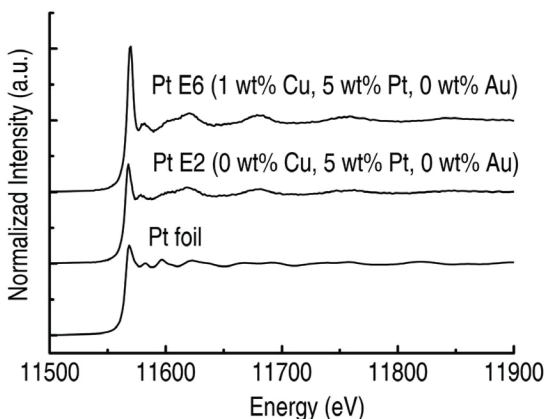


FIGURE 3. Pt L_3 -edge XANES spectra of samples E2 (just impregnated with PtCl_2) and E6, which contains Cu metal. Note the strong white line in this sample, indicating the presence of PtIV generated by the reduction of Cu^{2+} .

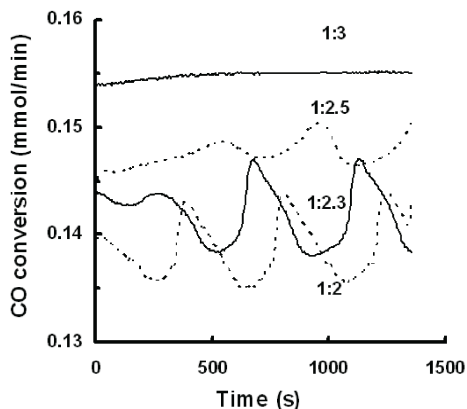


FIGURE 4. Oscillatory CO conversion over 1% Au/ Al_2O_3 at CO/O_2 ratios between 0.4 and 0.625.

Finally, illustrating one advantage of HT experimentation, namely serendipitous discovery, is that we found reaction conditions under which rate oscillations occur during CO oxidation over a number of Au catalysts (to our knowledge this is the first

report of oscillatory CO oxidation in the field of Au catalysis). As an example, Fig. 4 shows the rate oscillations over a 1% Au/ Al_2O_3 catalyst. The kinetic oscillations occurred in a 1:2 gas mixture and after a conditioning period of 6 h. Unfortunately, the acquisition of XANES spectra during the experiments was too slow to allow monitoring of the chemical state of the catalyst within one oscillation.

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