

High Throughput in Synchrotron Science: A New Approach in X-ray Absorption Spectroscopy

A. Beesley,¹ N. Tsapatsaris,¹ N. Weiher,¹ M. Tromp,² J. Evans,² A. Dent,³ I. Harvey,⁴ S. L.M. Schroeder^{1,5*}

¹ School of Chemical Engineering and Analytical Science, The University of Manchester, Sackville Street, Manchester, M60 1QD, UK; ² School of Chemistry, The University of Southampton, Highfield, Southampton, SO17 1BJ, UK; ³ Diamond Light Source Ltd., Diamond House, Chilton, Didcot, Oxfordshire, OX11 0DE, UK; ⁴ Synchrotron Radiation Source (SRS), Daresbury Laboratory, Warrington, Cheshire, WA4 4AD, UK; ⁵ School of Chemistry, The University of Manchester, Sackville Street, Manchester, M60 1QD, UK.

Introduction

The establishment of high-throughput (HT) methods in synchrotron radiation science can provide key strategies for the efficient use of synchrotron beam and with minimum human intervention [1]. In the catalysis community it is important to establish methods that facilitate the discovery and optimization of catalysts and the correlation of their electronic and geometrical structure with their catalytic performances [2,3]. This work presents a novel spectroscopic approach based on the combination of routine X-ray Absorption Spectroscopy (XAS) [4] with HT experimentation for quantitative electronic/structural characterization of catalysts precursors.

Methods and Materials

We have developed novel HT-XAS instrumentation that allows the elucidation of the atomic local structure [5] in a ternary Cu/Pt/Au library of supported catalysts precursors prepared by impregnation of γ -Al₂O₃ with aqueous solutions of CuCl₂, PtCl₂ and HAuCl₄. A SBS standard, 96 well-plate was used for the synthesis of a library of 91 catalyst precursors comprising compositional permutations of Cu, Pt and Au with different loadings. The HT-XAS setup is based on an in-house XYZ translation stage synchronized with the station computer through the TCP/IP protocol using a LABVIEW interface. XAS experiments at the Cu K, Pt L_{III} and Au L_{III} -edges were carried out at station 9.3 of the Synchrotron Radiation Source (SRS) at CLRC Daresbury Laboratory, UK. An in-house automated data reduction software based on the IFEFFIT [6] library was used to perform all necessary tasks of conventional XAS analysis. The software based on a series of Linux shell scripts which read sequentially, all the spectra in a subdirectory, applies the IFEFFIT background subtraction routine and perform the fitting analysis to a physical model. The script reports the shift on the edge position, the edge-step (ES) values, the normalized data, the $\chi(k)$ data, the Fourier transformed data, the fitting curves and the resulting fitted values for coordination number (CN), nearest neighbor distance (*R*) and Debye-Waller factor (σ^2).

Results

Fig. 1 shows some of the results obtained from the HT-XAS analysis. Each of these maps represents each of the 96 wells of the standard plate. From top to bottom the maps present the Pt concentration, ES and CN for each of the samples. Color black indicates either the absence of the metal under study or spectra with an extremely low S/N ratio. This HT-XAS analysis indicate that platinum in the precursors is present essentially in a 4-fold Pt-Cl coordination structure [7,8]. A comparison with reference spectra reveals that in some samples Pt is partially oxidized after impregnation [9]. All results of the automated analysis were additionally cross-checked individually, and it was found that the information provided by the maps was reliable. As a general trend, the automated analysis procedure generates low ES values for samples with poor S/N ratio,

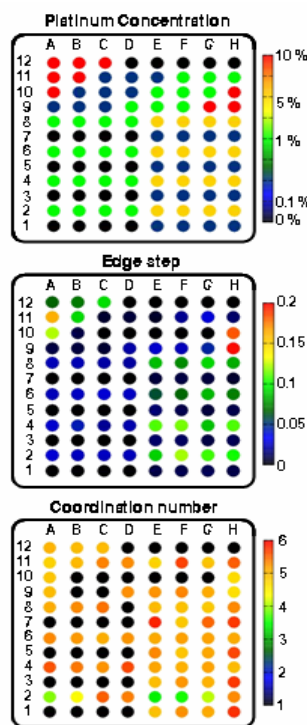


Fig. 1. Coloured representation of the Pt concentration (top), edge step (middle) and coordination numbers (bottom) obtained from the HT-XAS analysis.

which also corresponds to samples that contain low metal loading (*i.e.*, 0.1 wt%).

Discussion

Visual inspection of the figures immediately reveals the expected correlation between the metal concentration and the edge step values which supports the reliability of the HT analysis procedure. The CN values and the Pt concentration do not correlate as clearly, suggesting different local environments induced by the various metal concentrations present in the impregnated precursors. From the analysis of the data taken at the Cu K and Au L₃-edges we were able to perform immediate phase identification of the catalysts precursors as well as fast determination of instrumental limitations such as non-linearities on

the detector response as well as sample limitations based on the low ES values for low concentrated samples.

- [1] G. Bunker, N. Dimakis, G. Khelashvili, J. Synchrotron Rad. 12, 53 (2005).
- [2] C. Klanner, D. Farrusseng, L. Baumes, C. Mirodatos, F. Schuth, QSAR. Comb. Sci. 22, 729 (2003)
- [3] R. J. Hendershot, C. M. Snively, J. Lauterbach, Chem. Eur. J. 11, 806 (2005).
- [4] J. J. Rehr, A. L. Ankudinov, S. I. Zabinsky, Catal. Today 39, 263 (1998).
- [5] N. Tsapatsaris, A. Beesley, N. Weiher, M. Tromp, J. Evans, A. Dent, I. Harvey, S. Hayama, S. L.M. Schroeder to be submitted to J. Comb. Chem.
- [6] Newville, M. J. Synchrotron Rad. 8, 322 (2001).
- [7] R. Ayala, M. E. Sanchez, S. Diaz-Moreno, V. Sole, A. Munoz-Paez, J. Phys. Chem. B. 105, 7588 (2001).
- [8] B. Shelimov, J.-F. Lambert, M. Che, B. Didillon, J. Catal. 185, 462 (1999).
- [9] Yoshida, H.; Yazawa, Y.; Takagi, N.; Satsuma, A. Tanaka, T.; Yoshida, S.; Hattori, T. J. Synchrotron Rad. 6, 471 (1999).