

Microfocus XANES-CT, XRF-CT and XRD-CT on single catalyst particles before and during liquid phase hydrogenation

Stephen W.T. Price^{1*}, Andrew M. Beale^{2,3}, Tina Geraki¹, Konstantin Ignatyev¹, J. Fred W. Mosselmans¹

¹ Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxon, OX11 0DE, UK

² UK Catalysis Hub, Research Complex at Harwell, Harwell Science and Innovation Campus, Didcot, Oxon, OX11 0FA, UK

³ Department of Chemistry, University College London, 21 Gordon Street, London, WC1H 0AJ, UK

*corresponding author: stephen.price@diamond.ac.uk

The physicochemical state of a material is a key factor in determining catalytic activity and selectivity, however rarely are such materials structurally or compositionally homogeneous.^{1,2} Here we report on the 3-dimensional imaging of an industrial catalyst, Mo promoted colloidal Pt supported on carbon,³ both ex situ and during liquid phase selective hydrogenation reaction conditions. Initial ex situ studies concentrated on using microfocus X-ray fluorescence computed tomography (μ -XRF-CT), in combination with microfocus X-ray near edge spectroscopy computed tomography (μ -XANES-CT) to reveal details on the distribution of the chemical components present and their local coordination environment. Subsequently we show the initial results obtained from the recent development on the beamline of scanning μ -XANES-CT and μ -XRD-CT methodologies for chemical and phase imaging, in this instance for both the Pt catalyst and Mo promoter throughout the catalyst particle.

μ -XRF-CT reveals a distinct concentration of the Pt colloid on the surface of the carbon support as previously observed by FIB-SEM, however a lower concentration of colloid was observed to have diffused into the pores of the support, along with the Mo promoter (Fig. 1). Whilst XRF shows both species are well mixed on the micron scale, from extended x-ray absorption fine structure (EXAFS) measured on the catalyst ex situ reveal that there is no direct interaction between the Mo promoter and Pt, nor does this appear to change under reaction conditions, indicating that the promoter need only be in close proximity to improve both activity and selectivity. X-ray absorption near edge spectroscopy (XANES) (table 1) and EXAFS on the ex situ sample also reveal that the Pt colloids contain a mixture of reduced metallic Pt and Pt chloride species, neither of which are sufficiently crystalline to diffract. μ -XRF-CT under operating conditions reveals no change in the elemental distribution however the exposure to hydrogen is enough to cause the areas of highest Pt concentration to crystallize (Fig. 1). This crystallinity is confined to select regions on the surface of the support indicating that the majority of the Pt colloid is not crystalline yet still catalytically active.

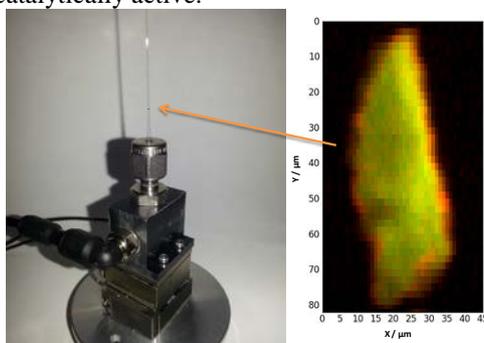


Figure 1. 0.5 mm diameter capillary cell for single particle catalysis (left) with vertical cross section from μ -XRF-CT (right) highlighting the variation Pt (red) and Mo (green) distribution.

Table 1. Component weightings from linear combination fitting of Pt L₃ edge XANES revealing local Pt coordination environment.

| Component | Weight | R _r | Reduced χ^2 |
|----------------------------------|---------------|----------------|------------------|
| Pt/C nano | 0.437 (0.017) | 0.0007 | 0.0001 |
| PtO ₂ | 0.094 (0.049) | | |
| PtCl ₂ | 0.207 (0.031) | | |
| K ₂ PtCl ₆ | 0.262 (0.026) | | |

Methodologies for μ -XRF-CT, μ -XRD-CT and μ -XANES-CT have been developed to allow for 3-dimensional imaging of elemental distribution, crystal phase and local chemical environment with 2 micron resolution. The design and construction of a capillary cell allow for this combined imaging to be performed under reaction conditions, including the heterogeneous catalysis of nitrobenzene to aniline.

We thank Diamond Light Source for access to beamlines B18 and I18 (proposal SP4939) that contributed to the results presented here, and the EPSRC for additional funding.

Refs

- 1) Beale et al. Coord. Chem. Rev. 2014 (in press) DOI: 10.1016/j.ccr.2014.05.008
- 2) J. Ruiz-Martinez et al. Angew. Chemie. Int. Ed. (2013), 52, 5983.
- 3) E. Boymans, S. Boland, P. T. Witte, C. Mueller and D. Vogt, Chemcatchem, 2013, 5, 431-434.