

Sample Preparation and Analysis of Aggregated ‘Single Atom Alloy’ Nanoparticles by Atom Probe Tomography

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Atom probe tomography (APT) is a powerful technique for the characterization of composition of materials and their three-dimensional structure down to the atomic-scale. With the new developments in FIB-based sample preparation, there is a growing interest in the analysis of catalytic systems by APT [1]. Our current research focuses on the use of nanostructured materials for sustainable catalysis applications, and more specifically, on metallic alloy catalyst materials for selective oxidation or dehydrogenation reaction. The principal design feature of the catalyst material is to combine a minor amount of active metal that facilitates creation of reactive intermediates with a less active majority phase that transforms these intermediates to desirable products with high selectivity.

Copper-based catalysts, in the form of single atom alloy (SAA) catalysts, are currently being developed for selective dehydrogenation reactions using a modified electroless galvanic deposition method [2]. CuNi_{0.01} nanoparticles were synthesized on graphite to avoid the presence of a porous support which may affect the 3D reconstruction. The incorporation of atomically dispersed Ni within Cu catalysts (as both nanoparticles and nanoporous structure) allows lowering the activation energy for dehydrogenation of alcohols. The typical concentration of Ni on these supported CuNi nanoparticles is 0.01 or 1 % atomic, and it is difficult to localise the Ni atoms with regular microscopy techniques. APT should be particularly suited to determine the distribution of Ni within the nanoparticles.

The different pathways for the preparation of atom probe samples from nanoparticles consist mainly in dielectrophoresis, drying/incubation, and agglomerate lift-out (in the case of powder samples) [3]. However, after reduction in H₂, the catalyst appears in the form of isolated 12-15 nm nanoparticles and agglomeration of nanoparticles into 1-3 μm clusters (see Figure 1(left)). It has to be noted that the dispersion of nanoparticles is too low to use the drying/incubation techniques. To prepare samples suitable for APT analysis, clustered nanoparticles were attached to an *Omniprobe* tip with Pt-weld in the FIB, and the agglomerate was then sharpened down to a radius of ≈50 nm. The agglomeration of NPs induces the formation of a porous structure, which has been filed with Pt-weld at every step of the sample preparation (before and after annular milling) to avoid as much as possible the presence of aberration and sample fracture due to the presence of porosity.

Fresh catalysts (before any reaction) were analysed by APT. Experiments were performed in a LEAP 4000X HR system with conditions of acquisition: 40 pJ, 100 kHz, 50 K, DR: 0.25%. Even though the structure has been filled as much as possible, the presence of voids in the agglomerate is inevitable, and induces micro-fractures which are reflected in the voltage plot. As it can be seen on Figure 1(right), the 3D reconstruction displays the presence of ≈15 nm particles. The mass spectrum indicates the presence

of Cu, CuH and Cu_xO_y species. The copper hydrates are due to the initial pre-treatment, and the copper oxides are believed to be due to the exposure of the sample to air after FIB. To determine the presence of Ni and/or the presence of clustering in this sample, further data treatment has been performed, as well as comparative STEM-EELS measurements.

In conclusion, this study has proved that, even though the structure is not optimal, it is possible to prepare APT samples from agglomeration of nanoparticles using a rather fast technique, which does not require deposition and incubation of the nanoparticles. This procedure could also be used in future developments towards the analysis of porous materials by atom probe tomography. Future research will focus on the study of SAA catalysts on different supports, as well as the evolution of the composition at different steps of the catalytic reaction [4].

References:

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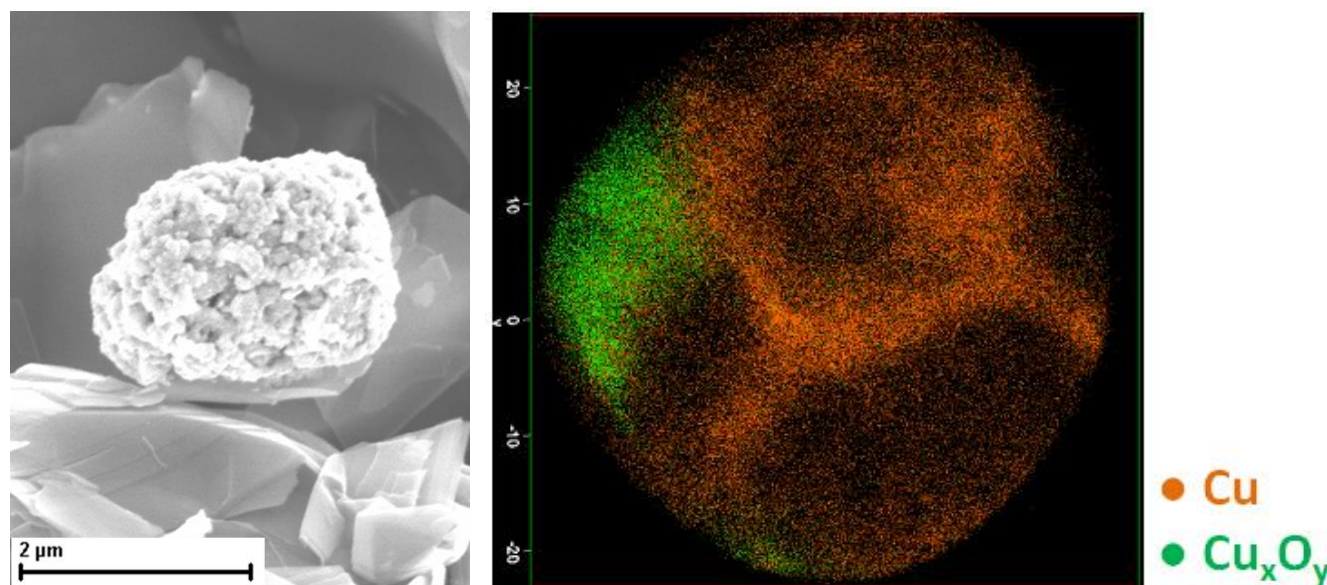


Figure 1. (left) SEM image of the agglomeration of SAA catalyst nanoparticles supported on graphite - (right) APT reconstruction: 2D projection of a selected region of the sample allowing discerning the presence of nanoparticles, and showing the partial oxidation of the sample (scale is in nm)