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Z-contrast imaging as a tool for atomic level analysis of bimetallic structures

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Intensity on the HAADF-STEM micrographs is sensitive to atomic number and has been used by many researchers to obtain quantitative information on the morphology and chemistry of nanostructures [1]. Absolute quantification of the intensity is a tedious process which requires multiple time-inefficient steps to calibrate the measured intensity as accurately as possible [2, 3]. Nevertheless, researchers have successfully quantified the structural parameters of sub-nanometer clusters on crystalline metal-oxide supports [4, 5]. Browning et al. used dynamic multislice STEM imaging simulations to determine the morphology of bimetallic nanostructures on crystalline MgO [5]. This method heavily relies on the well-defined metal-oxide surface where long range-order of the crystalline as well as the uniform thickness of the support helps to quantify the structure. There is great interest for methods to work on not so ideal structures.

The goal of our work is to expand the HAADF-STEM quantification on less-ideal structures, where the support thickness is not uniform and no long-range order exists within the structure. HAADF-STEM intensity will be used on these rough surfaces to differentiate between atoms of different elements. This work is demonstrated on an alumina surface where the structure is porous and the surface is rough. The metals are chosen as Pt and Pd to exploit the Z-difference between Pt atom (Z=78) and Pd atom (Z=46) resulting in a significant contrast difference on HAADF-STEM imaging. Catalyst materials make a good model for this study, as Pt-Pd form sub-nanometers sized clusters on Al_2O_3, which makes the structural analysis easier as there are fewer atoms reducing the number of possible configurations considerably.

Previously, we have reported elemental analysis and morphological evaluation based on the HAADF-STEM intensity profiles [6]. Here, the analysis is based on area quantification of the intensities. A HAADF-STEM micrograph is shown in Figure 1A. The micrograph contains a sub-nanometer cluster and an individual atom. Then 3D intensity map of the micrograph is plotted in Figure 1B. The intensity of the cluster and atoms are circled by the blue ring and green rings respectively. The total intensity of the single atom is measured by cumulatively summing up all intensity values encircled within the boundaries that define the atom (Figure 2). To remove the signal contribution of the background intensity, a region is defined around the atom to define the background and its cumulative signal intensity is subtracted from that of the atom after normalizing the intensity value to the area of the atom. The obtained intensity is used as an internal reference for single atom intensity. The intensity of the cluster is obtained in a similar fashion by defining the areas for the cluster and background and calculating the background subtracted intensity of the cluster. The cluster intensity value is used to determine how many atoms each cluster comprises and to assess the number of layers in the clusters.

For this study, the Pt on Al_2O_3 is used as a control sample. The clusters on both the Pt/Al_2O_3 and $Pt-Pd/Al_2O_3$ are found to possess a bilayer structure by the area intensity analysis. Individual atoms on the bimetallic sample have analyzed and a higher fraction of atoms were found to be Pd. STEM-EDX suggested the clusters to be Pt-rich. Given the Pd-rich bulk loading of the sample, the presence of Pt-rich clusters further supports the higher fraction of Pd single atoms.

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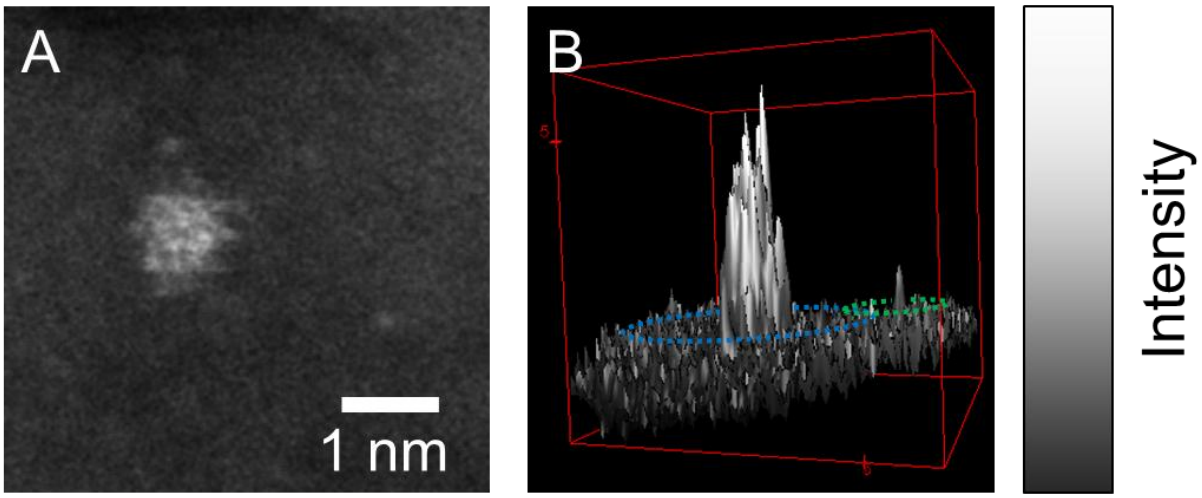

Figure 1. (A) HAADF-STEM micrograph of the Pt:Pd/Alumina catalyst (B) HAADF-STEM intensity map of the micrograph in (A)

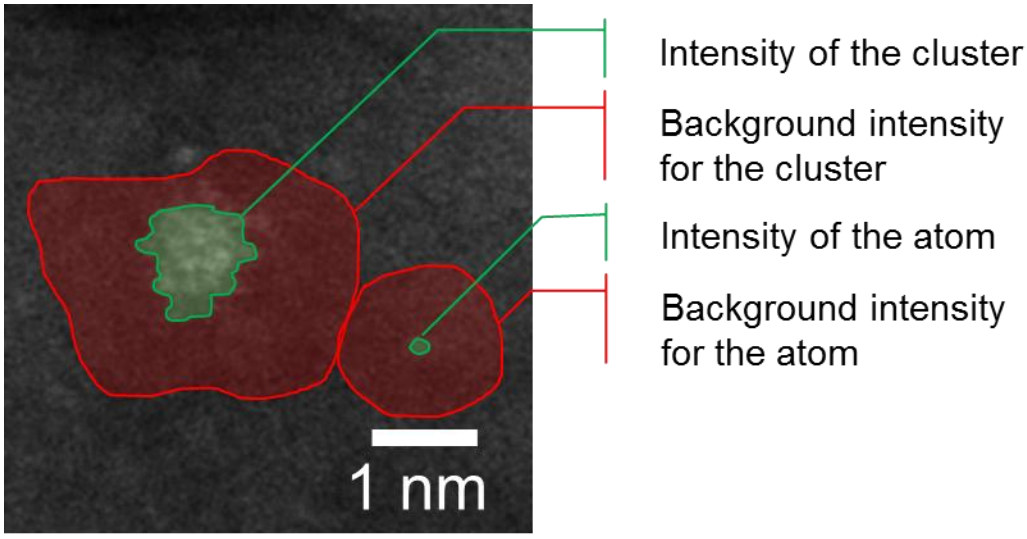

Figure 2. Regions are defined around structures of interest to determine the intensity coming from the signal and the background

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