

Atomic Level Element Specific Investigation of Bimetallic Structures by Z-Contrast Imaging

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The sensitivity of HAADF-STEM to atomic number has been used to obtain quantitative information about the structure and chemistry of nanostructures. Electron tomography based on Z-contrast has been used to obtain atomic resolution 3D reconstruction of crystalline nanoparticles [1]. This approach needs two or more projections of the structure that are later processed computationally by discrete tomography to determine the position of each atom in space. This method utilizes crystallographic constraints of the structure and would be of limited use for structures lacking long-range order. Browning et al. utilized quantitative Z-contrast imaging to resolve the structure of sub-nanometer clusters on crystalline metal-oxide support [2]. The group has utilized dynamic multislice STEM imaging simulations which greatly benefit from the well-ordered crystalline support of uniform thickness. This method would be of less use on support materials of varied thickness with complex crystal structure. Another setback of this method constitutes itself where quantitative imaging requires calibration of the intensity levels to compensate varying experimental parameters. Different groups have developed theories and best practices to quantify the intensity as accurately as possible, requiring tedious and time-inefficient steps [3, 4].

Our work focuses on the use of Z-contrast imaging to obtain structural and element specific information on sub-nanometer clusters supported on rough surfaces without the need of absolute intensity calibration. The goal is to specify the elemental nature of an atom by differentiating its intensity level from other possible elements. This capability is demonstrated on a Pt-Pd catalyst supported on Al_2O_3 using an aberration-corrected, sub-Ångstrom resolution scanning transmission electron microscope. This system was chosen as Pt atoms ($Z=78$) are 1.7 times heavier than Pd atoms ($Z=46$) resulting in significant contrast difference to be utilized by HAADF-STEM imaging. Further, the studied material has sub-nanometer average cluster size, which simplifies deciphering structure, as clusters composed of fewer atoms have less configuration possibilities. Single atom elemental identification is performed by referencing the lowest atom intensity as Pd and categorizing other atoms based on their intensity relative to the reference atom for each micrograph. Cluster morphology is determined by quantifying the intensity profiles of the clusters with respect to the reference atom. Chemistry of the clusters is estimated based on possible configurations that would satisfy the observed morphology for the existing elements.

Pt on Al_2O_3 is used as a monometallic control sample. The micrograph shown in Figure 1A illustrates Pt atoms along Pt clusters. The cluster is determined to possess a bilayer structure (Figure 1B). Al_2O_3 supported Pt:Pd (1:1 by weight) catalysts are imaged by aberration corrected STEM (Figure 2A). An example of the results is shown in Figure 2B comparing the intensity profiles of a single atom along with two clusters, one of which is approximately twice as large as the other. The fraction of single Pd atoms is determined by the previously described method for a series of micrographs. The Pt:Pd sample exhibited a higher fraction of single Pd atoms compared to single Pt atoms. The chemical nature of the clusters is also estimated with the aforementioned method and cross-checked by STEM-EDX measurements, both of which found the clusters to be slightly Pt rich. By its bulk loading, the bimetallic sample has 80% more Pd than Pt atoms. Based on this, Pt rich clusters would imply that higher fraction of the single atoms will be Pd, confirming the aforementioned finding.

- [1] Van Aert et al, Nature (2011), 470 374–377
 [2] Browning et al., ChemCatChem (2013), 5 2673 – 2683
 [3] LeBeau et al, Ultramicroscopy (2008), 108 1653–1658
 [4] Yang et al, Materials Characterization (2003), 51 101– 107

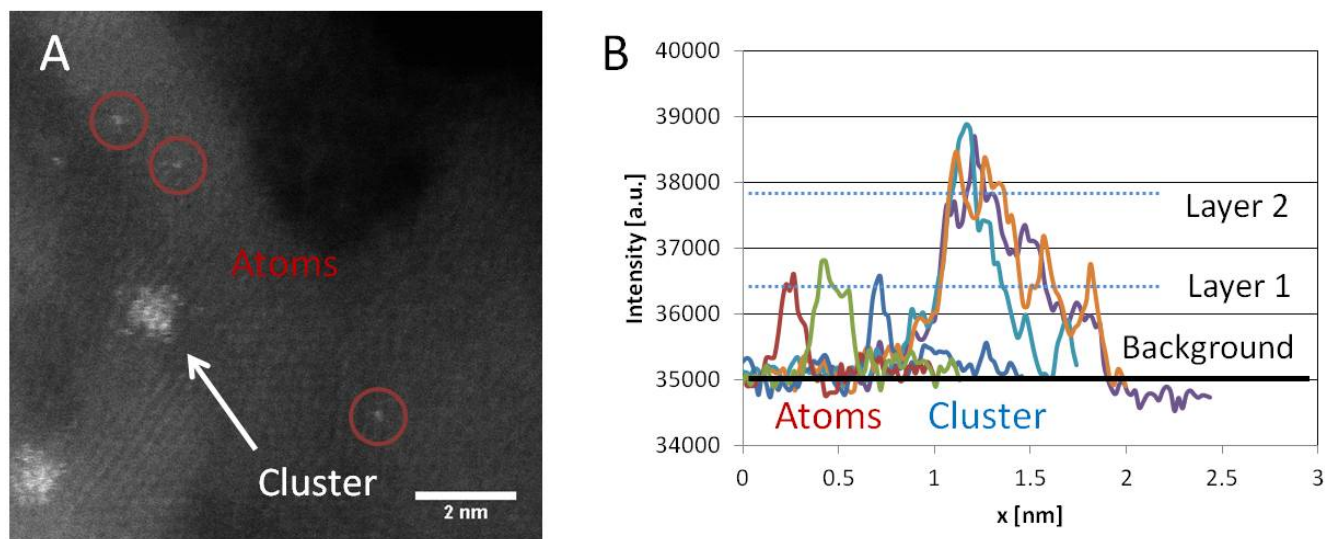


Figure 1. (A) HAADF-STEM micrographs of the Pt/Al₂O₃ catalyst (B) HAADF-STEM intensity profiles of atoms compared to the line profiles obtained from the cluster. The dashed lines indicate to the unit thickness and its multiples.

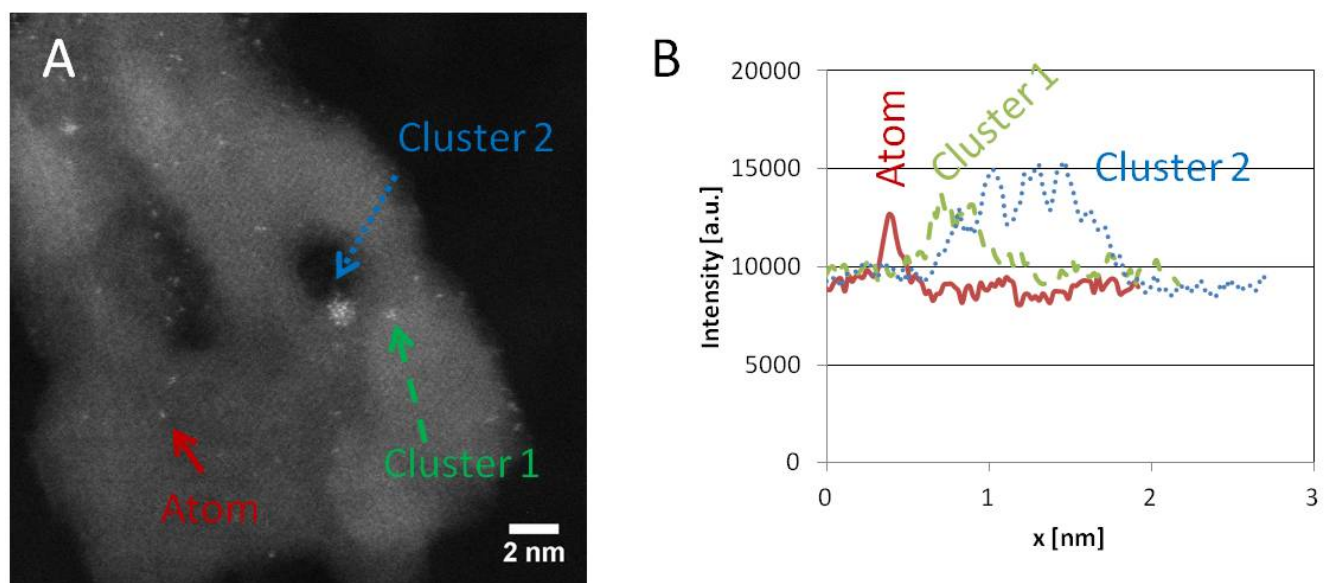


Figure 2. (A) HAADF-STEM micrographs of the Pt/Pd/Al₂O₃ catalyst (B) HAADF-STEM intensity profiles of various structures