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Identifying Individual Atoms in Single Atom Pt/CeO_2 Catalysts

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Single-atom catalysts have recently attracted a lot of attention because of their unique reactivity and atom efficiency, which becomes very important for scarce platinum group metals. Heterogeneous catalysts consist of nanoparticles on oxide supports. Only a fraction of the total number of atoms in a nanoparticle are located on the surface, hence those atoms in the bulk are wasted since they do not participate in the catalysis occurring at the surface. If the precious metal is atomically dispersed on a support, every atom can participate in the chemical reaction. Aberration corrected STEM imaging has been responsible, in part, for the growing interest in this field, since these isolated metal atoms can now be imaged [1].

Figure 1a shows a typical AC-STEM image from a single atom catalyst, in this case 3 wt% Pt/CeO_2 whose synthesis and catalytic activity has been described previously [3]. The region marked A shows strong contrast from the ceria support because it is oriented close to the [112] zone. The dominant contrast from the Ce cations makes it difficult to find the isolated Pt atoms. Other parts of the image where the ceria particle is oriented away from a strongly diffracting position allow us to see the Pt atoms. The individual Pt atoms can be recognized and counted (25 atoms are located in the 5nmx5nm box shown in Figure 1a), and as shown in previous work, and the number of bright dots (Pt atoms) per unit area, match with the total Pt loading (~1 atom/nm^2) [3].

While isolated atoms are visible, it is not possible to confirm their identity. Here we present an approach that uses the intensity of the cations in the support to serve as a reference, allowing us to confirm that a bright dot is indeed a Pt atom. Our method relies on finding regions of the sample that are oriented away from a low index zone, so that individual cations of the support become visible as shown in Figure 1b. Figure 1b shows a Ce lattice along the [110] zone where each lattice position represents a column of atoms. Figure 1c shows how a ceria crystal, tilted away from the [110] zone now shows a row of Ce cations at an angle to the (111) lattice plane. The spacing of Ce atoms is such that these individual atoms can be resolved using the sub-nm probe possible in AC-STEMs such as the JEOL NeoARM with the URP polepiece that was used in this work. In such an image, it is now possible to determine the intensity of individual ceria cations, which can be used as a reference to identify single Pt atoms.

The method used is similar to that of previous work where a column of Pt atoms was analyzed to determine the number of Pt atoms within a nanoparticle [2]. Isolated Pt atoms such as those seen in the single atom catalysts (Fig. 1a) have not been quantitatively analyzed thus far. This is because there is no easy reference available to analyze the intensity of the bright dots in an image such as shown in Fig. 1a. In a previous study [4], isolated atoms of La were used as a reference to confirm the presence of single Pd atoms in a Pd/La-Al_2O_3 catalyst. Here we are able to utilize the catalyst support as a reference by examining images off the zone axis which yield individual Ce atoms as reference, allowing us to reliably confirm the identity of individual Pt atoms in this catalyst.

We use an approach like that used in previous work [2][4] which involves fitting a two-dimensional (2D) Gaussian function to the bright objects being studied, which in our case correspond to individual atoms. Since HAADF-STEM image contrast is dominated by Rutherford scattering, the intensity is proportional to Z^2.

A sample containing 3 wt% Pt on polyhedral ceria was imaged by HAADF-STEM and a particle tilted off the [110] zone was studied (Figure 2a). Next, intensity maps of areas of interest were created to ensure the

data to be fit. This was done using a commercial software program Origin Pro (Figure 2b-c and 2e-f). A 2D Gaussian fit was then applied to the intensity maps (Figure 2d and 2g). The height of the Gaussian peak was used to infer the intensity of each atom. We applied this method to the thinnest region of the sample, so no background subtraction was necessary. Region 1 in Figure 2a contains only Ce cations while region 2 contains a brighter atom in addition to the Ce cations. By using the intensity of the Ce cations as a reference, the intensity of the brighter atom can now be assessed. Comparison of the intensities suggests that the measured intensity ratios are in good agreement with the square of the atomic number (Ce Z=53, Pt Z=78). The expected intensity ratio was 0.55 while the intensity ratio from the 2D Gaussian fit was found to be 0.54. This allows us to confirm that the bright dot in box 2 is indeed a Pt atom.

Industrial catalysts contain multiple metals, for example Pt and Pd, and it would be important to know if they are located in close proximity and their arrangement with respect to the support metal cations. Our approach here, of looking at a crystal lattice and using the cations in the support, provides an opportunity to study and quantify individual atoms, not just atom columns as has been done in previous work. Future work will involve refinement of the approach to allow background subtraction so that the large number of Ce cations seen in this image can be analyzed and used as reference to refine the identity and location of individual atoms present in thicker regions of this image. Our approach uses a commercially available Origin PRO software where no additional programming is needed, which makes this approach more broadly applicable.

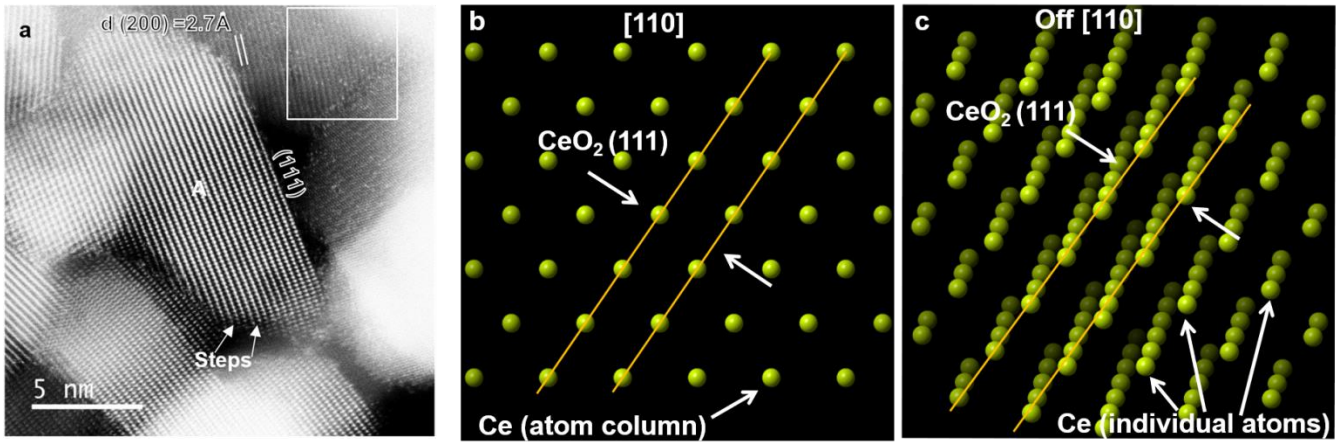

Figure 1. Figure 1: a) AC-STEM image of 3 wt% Pt/CeO2 prepared via atom trapping. Particle A is oriented along the [112] zone axis resulting in strong contrast from the Ce atom columns, while the ceria particle in the boxed region is oriented off the zone axis making it easier to detect the Pt single atoms, which appear as bright dots. The boxed region is 5 nm× 5 nm in size and contains 25 Pt atoms, consistent with the overall loading of 1 Pt atom/nm2. Surface steps are a common feature of ceria polyhedral particles and are likely sites for strong binding of Pt single atoms. The figure content is adapted with permission from Kunwar et al. [3]. Copyright (2019) American Chemical Society. b) Ceria crystal oriented along the [110] zone where the arrow points to a Ce cation which represents a column of Ce cations. c) Ceria crystal tilted away from the [110] zone where each individual Ce cation can be seen.

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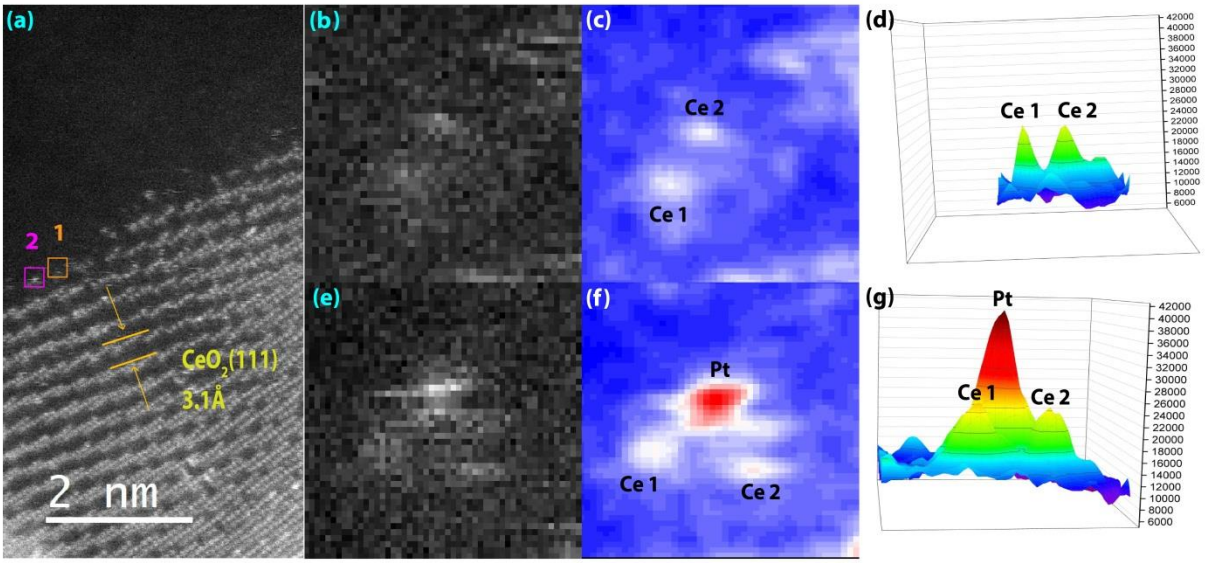

Figure 2. Figure 2: This image was obtained from the same 3 wt% Pt/CeO2 catalyst described in Figure 1. (a) A typical image from this sample oriented off the [110] zone axis where individual Ce cations can be seen as described in Figure 1c. Two regions of this sample labeled 1 and 2 were analyzed. (b,e) Shows the magnified grayscale image for regions 1 and 2, respectively. (c,f) Colorized intensity maps of regions 1 and 2, respectively. (d,g) Two-dimensional (2D) Gaussian fit to intensity map in (c) and (f), respectively. These fits show well resolved peaks corresponding to the intensity of Ce and Pt individual atoms. The intensity ratio agrees with that expected based on the atomic number.

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