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The Dynamic Shape of Ceria Nanoparticles

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Cerium-based oxides constitute an important class of catalysts that can exchange oxygen rapidly under variable reducing or oxidizing conditions. This property, characterized as the oxygen storage capacity (OSC), has made it a material of considerable interest in applications such as automotive exhaust clean-up, in gas sensors, and in fuel cells electrodes. A significant fraction of the associated non-stoichiometry, mainly caused by valence changes of the cerium ions with formation or elimination of oxygen vacancies,[1-4] may be accommodated in the surface layer of the nanosized catalyst particles, accompanied by nanoparticle shape changes. Here we show by direct atomic imaging the dynamic surface rearrangement of cerium ions on ceria nanoparticles, likely accompanied by oxygen loss, during *in situ* observation in an atomic resolution transmission electron microscope. Such surface reconstruction may have an important role in the catalytic activity of ceria on redox cycling and in its effectiveness as fuel cell electrode catalysts, by the dynamic formation of catalytically active sites.

High surface area ceria samples were synthesized using wet chemical method. Atomic level observations of surface reconfiguration taking place under electron beam illumination were carried out in a JEOL 2100 transmission electron microscope. The intensity of electron beam was estimated at approximately $15Acm^{-2}$, with the <011> parallel to the beam. *In situ* high resolution electron microscopy (HREM) images were employed to monitor the changes in particle morphology and structure, and electron energy-loss spectroscopy (EELS) was used to follow the oxidation state of Ce. The image simulation was used to determine the structure of the reduced phase induced by electron beam illumination.

Figure 1 shows sequential atomic-level images of dynamic surface reconstruction for a nearly octahedral ceria nanocrystal under electron beam illumination. The atomic resolution images represent two-dimensional projections of the atom columns, so that this nanoparticle appears as a truncated parallelogram with 14x13 (cerium) columns (dark spots), initially. Dynamic configurational changes are evident, especially at the corners and edges projections. For this thin specimen (weak phase object) at “optimum defocus”, image simulations using the multislice method indicate that the dark dots in the images indeed correspond to Ce atoms or atom columns. Here we focus on the <110> edge projection A and the {111} facet projection between A and corner B. After 17 minutes of electron beam illumination, several atoms have been removed from corner B, while the Ce ions at edge A have also relocated, a start of a reconstruction that leads to the formation of a {100} facet truncation at B, and a small {022} facet formation at A after 79 min. Then, atoms on the {111} facet between A and B progressively relocate upon continued observation. After 98 min the projected number of atom columns on this facet have decreased significantly, and relocation is complete just 3 min later. This dynamic shape evolution is consistent with the expectation that the atoms located at corner and edge or terrace ledges are structurally less stable, or more active, sites in nanoparticles due to their low coordination number. After this, min 101, continued surface Ce-atom motion can be observed starting from the newly formed surface. The projected particle now has

12x14 atom columns. A reasonable hypothesis is that these atoms have relocated to {111} surfaces of the octahedrally-shaped nanoparticle.

References

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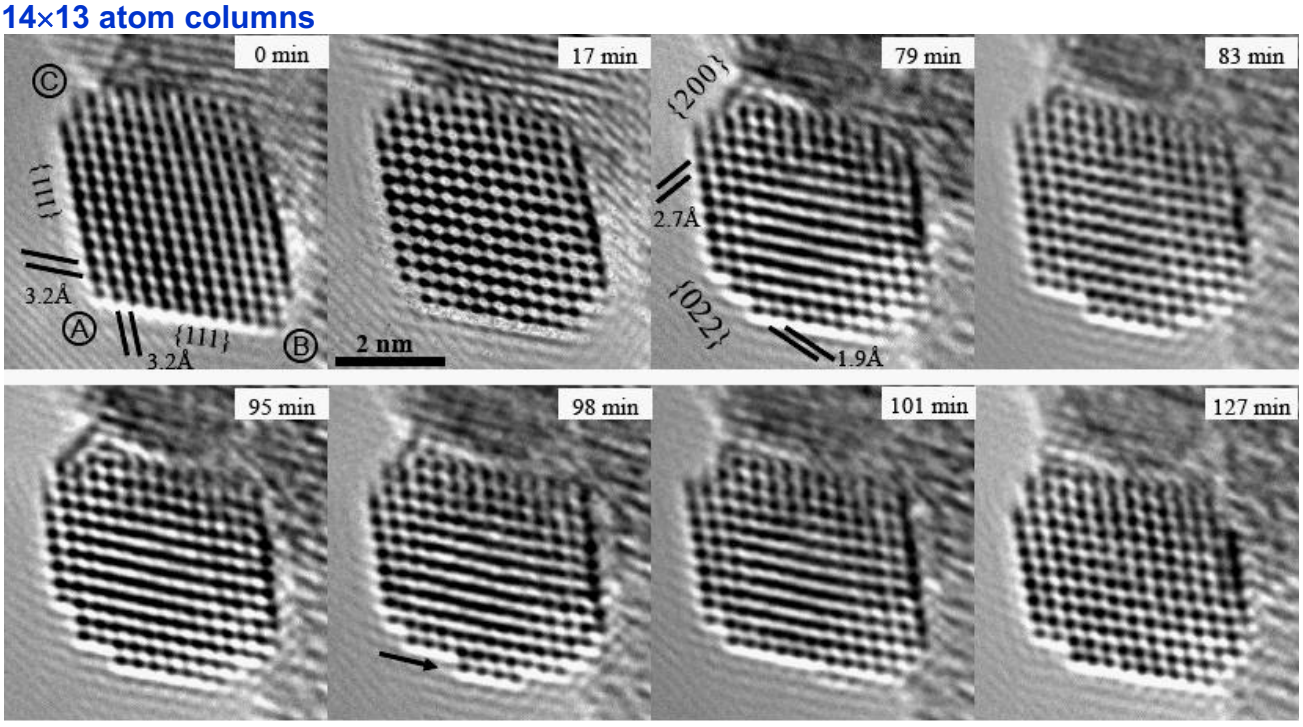

Figure 1. Dynamic surface reconstruction of a ceria nanoparticle. The images were acquired *in situ* in a TEM under electron beam illumination. The significant dynamic changes were observed *in situ* at positions A, B, and C, and are especially clear at corner A and at the edge (or surface) between A and B.

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