

## Application of 4D STEM and DPC Techniques to Study Surface Reconstruction of Transition Aluminas

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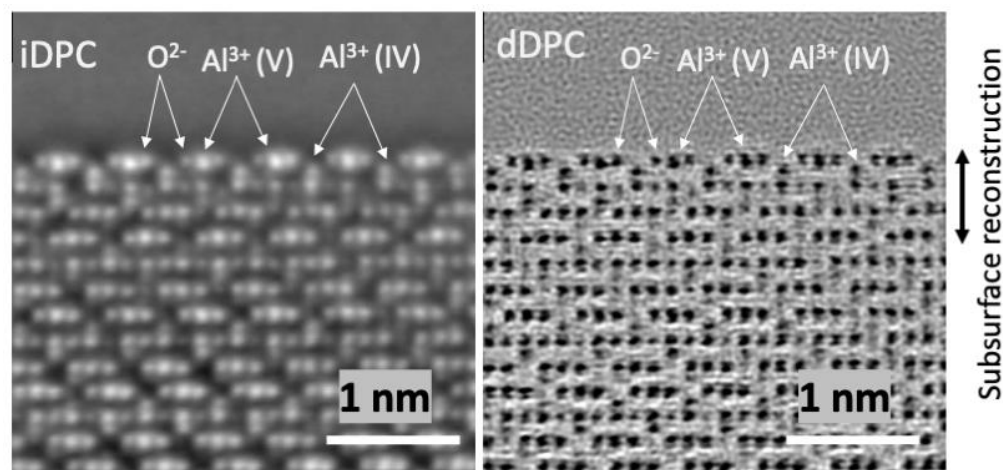
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Transition aluminas are used in catalytic applications as catalysts and catalytic supports due to their excellent thermal stability, ability to maintain high surface area, and most importantly their unique surface properties [1]. Understanding the surface properties of transition aluminas has been the subject of extensive research, and while much progress has been made, the actual surface structure of transition aluminas remains only conceptually understood [1,2,3]. A detailed nature of bonding environment has been mostly inaccessible to surface science techniques because of high degree of structural disorder, as well as inherent difficulties associated with studying high surface-area materials.

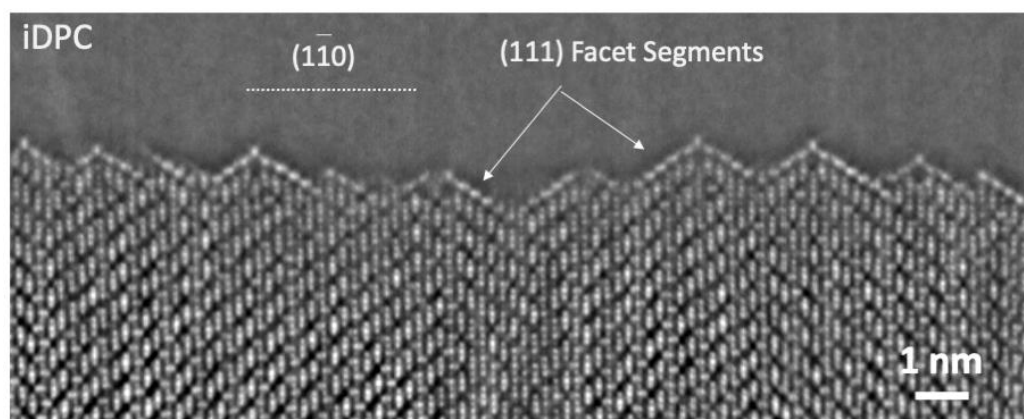
In this work, we will present results from atomic resolution STEM imaging of surface structures of transition aluminas as enabled by segmented and pixelated (EMPAD) detectors. Our observations focus on important low index surfaces, as well as irrational surfaces, of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> and  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. These are high temperature phases of transition aluminas. The microstructural observations were performed with aberration corrected Thermo-Fisher Scientific Themis Z 30-300, operated at 300kV, and using complementary HAADF, Differential Phase Contrast techniques (iDPC, dDPC) and Center of Mass (iCoM, dCOM) imaging techniques.

Low index (100) surfaces represent one of the main terminations of transition aluminas. An example of (100) surface of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> as obtained with iDPC and dDPC imaging is shown in Figure 1. The images reveal the details of oxygen and aluminum sublattice and based on the analysis of symmetry and relative intensities, it will be shown how the (100) surface undergoes complex reconstructions. The key feature of (100) surfaces are densely populated rows of pentacoordinated Al<sup>3+</sup> sites. At subsurface region, within ~0.5 nm, we identify multiple modifications at octahedral and tetrahedral Al<sup>3+</sup> sites, indicating complex subsurface reconstructions. The (100) surface in Figure 1 has been identified as one of several possible surface structures. Other types will be presented, and it will be shown how the intergrowth nature of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> itself supports different structures and terminations. In addition to (100) surfaces, our presentation will also focus on (110), (111) and other types of irrational surfaces. An example of (110) surface of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> as revealed with iDPC is shown in Figure 2. In this case, the surface undergoes extensive reconstructions by splitting into (111) facets. The nature of surface sites for this and other surfaces will be presented in the context of overall structural models.

As a part of this work, we will discuss challenges associated with studying the surfaces of transition aluminas, including challenges associated with electron beam damage and challenges related to thickness requirements for phase contrast imaging techniques [4].



**Figure 1.** (a) Atomic level view of (100) surface of  $\delta$ - $\text{Al}_2\text{O}_3$  as obtained with iDPC and dDPC imaging.



**Figure 2.** STEM iDPC image of (110) surface of  $\delta$ - $\text{Al}_2\text{O}_3$ . The (110) surface undergoes reconstructions as it splits into two (111) facets that host several unique surface sites.

#### References:

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- [2] Kovarik, L., Bowden, M., & Szanyi, J. (2021). *Journal of Catalysis*, 393, 357-368.
- [3] Khivantsev, K., Jaegers, N. R., Kwak, J. H., Szanyi, J., & Kovarik, L. (2021). *Angewandte Chemie*, 133(32), 17663–17671.
- [4] This research was performed at the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at PNNL. It was supported by the U.S. DOE, Office of Basic Energy Sciences, Division of Chemical Sciences, Biosciences and Geosciences.