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In-situ Observation of Ordering Transformations in θ-Al_2O_3

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Metastable polymorphs of Al_2O_3 (transition aluminas) are heavily used in catalytic applications due to their advantageous thermal and surface properties [1]. In the group of transition aluminas derived by thermal decomposition of boehmite, there are three known polymorphs denoted as γ-Al_2O_3, δ-Al_2O_3 andθ-Al_2O_3. The polymorph of θ-Al_2O_3 is the most stable transition alumina, forming only at the highest temperatures (950-1050°C) by transformation from γ-Al_2O_3 and θ-Al_2O_3 [2-4]. Because of the highly defective and disordered nature of the earlier forming polymorphs, the mechanism of θ-Al_2O_3 formation remains poorly understood. In the current study we present *in-situ* TEM heating studies aimed at revealing the mechanism of θ-Al_2O_3 formation.

The microstructural observations were performed with a probe corrected FEI Titan 80-300. The image collection was done in Scanning Transmission Electron Microscopy (STEM) mode using a HAADF detector at 300kV. Selected samples were heated *in-situ* using a double tilt Aduro Protochips heating holder. The heating experiments were performed at 1000-1100°C, and the observations were performed at room temperature after each successive heat treatment in order to minimize beam damage. The observations allowed us to track the evolution of microstructure for individual particles at the atomic level.

For boehmite derived samples, the decomposition is traditionally considered to proceed in the sequence of γ-Al_2O_3 → δ-Al_2O_3 → θ-Al_2O_3. In our presentation, it will be shown that the decomposition of γ-Al_2O_3 to θ-Al_2O_3 can proceed directly through the formation of a highly disordered precursor state that is denoted as θ′-Al_2O_3. The formation of such a disordered state is accompanied by the formation of δ-Al_2O_3, which is often the main component of the evolving microstructure. An example from 1000 °C heat-treated microstructure accommodating both phases is shown in Figure1. θ′-Al_2O_3 can be recognized from a series of non-periodically distributed high intensity features (fully occupied octahedral sites), which can be rationalized as δ-like defects embedded within the crystal of θ-Al_2O_3 considering β-Ga_2O_3 structural type.

Upon further heating at 1000 °C, the microstructure of θ′-Al_2O_3 undergoes ordering before it transforms to θ-Al_2O_3. An example of an ordering transformation after additional 20-minute heat treatment at 1000°C is shown in Figure 2. Multiple periodicities can be identified within the more ordered segments. The interpretation of such a structural state can be provided as a linear combination of monoclinic crystals with A2/n space group, which are related to δ-Al_2O_3 and θ-Al_2O_3 (considering the structure of β-Ga_2O_3). The final transformation to θ-Al_2O_3 involves a reduction of number of δ-like defects, but even after prolonged high temperature treatment, as found through a combination of ex-situ and in-situ heating experiments, the defects are not eliminated. The residual amount is expected to be entropically stabilized. As a part of this work, we will discuss the role of θ′-Al_2O_3 in the formation of θ-Al_2O_3, and show how the new observations can help to rationalize the often-observed slow kinetics of δ-Al_2O_3 to θ-Al_2O_3 transformations [5].

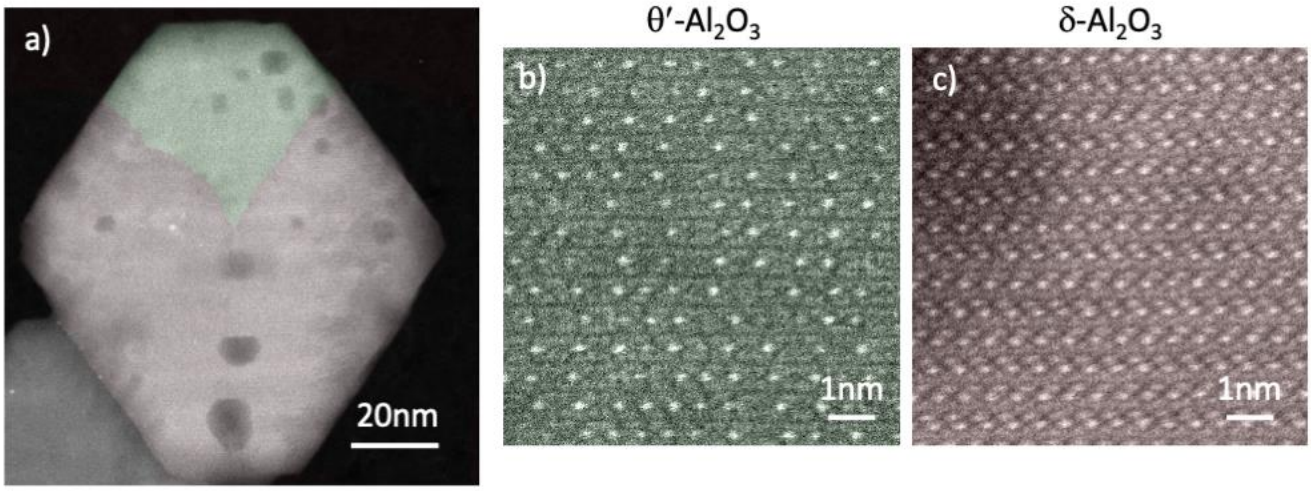

Figure 1. (a) Particle of transition Al2O3 studied during in-situ heating at 1000 °C. The microstructure evolves to (b) disordered precursor state of θ-Al2O3 and (c) planar intergrowth structure of δ-Al2O3.

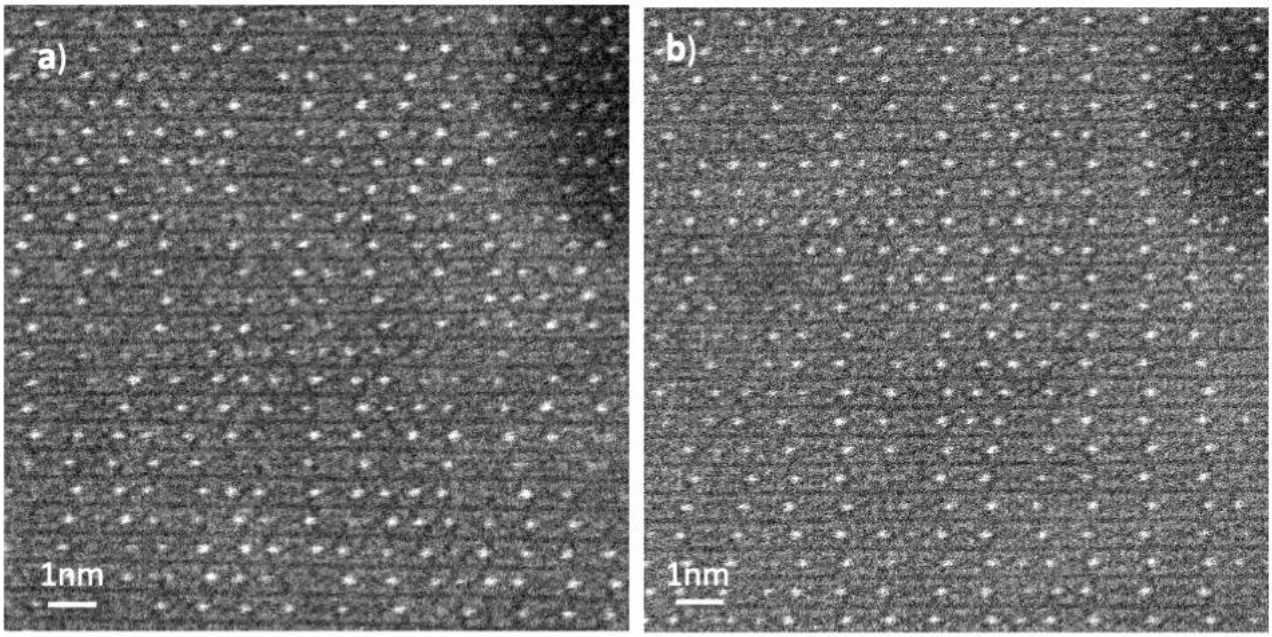

Figure 2. Evolution of θ′-Al2O3 during in-situ heating: (a) θ′-Al2O3 heated to 1000 °C, (b) ordering within θ′-Al2O3after additional heating for 20 min at 1000 °C.

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