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Towards Atomic Level Understanding of Transition Alumina Phases and Their Phase Transformations

L. Kovarik[1], M. Bowden[1], D. Shi[2], A. Anderson[1], Jianzhi Hu[2], J. Szanyi[2], J. H. Kwak[3], C.H.F. Peden[2]

[1] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington USA
[2] Institute for Integrated Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington USA
[3] School of Nanobiotechnology & Chemical Engineering, UNIST, Ulsan 689-798, Korea

Transition Al_2O_3 derived from dehydration of Al hydroxides are highly complex materials with a significant degree of inherent structural disorder. The way in which the disorder is manifested for various heat treatment conditions and for various hydroxide precursors is a highly relevant topic in catalysis, with important implications for rationalization of unique surface chemistry and catalytic behavior of these materials [1]. When heat-treated at relatively high temperatures (>900°C), the complexity of the microstructure is generally associated with the polymorphs of δ-Al_2O_3 and θ-Al_2O_3, which form in closely inter-growing structures. This has been a main issue in their reliable characterization, and there are currently none or only poorly fitting crystallographic models available. Similarly, the stability of these polymorphs remains poorly understood and actively studied [2].

In this work we address the structural nature of δ-Al_2O_3 and θ-Al_2O_3, and the mode of their phase transformations using combination of *in-situ* and *ex-situ* imaging and spectroscopy techniques. The current work mainly relies on the use of HAADF Scanning Transmission Electron Microscopy imaging, XRD, high-resolution NMR and DFT calculations. The HAADF STEM observations were performed with a probe corrected FEI Titan 80-300, and the thermal treatment was performed under *in-situ* heating conditions inside the TEM with Aduro Protochips heating holder at 900-1100 °C.

Figure 1 shows structural and morphological changes that occur during heat-treatment of transition Al_2O_3 particles. The in-situ observations enabled us to characterize the evolution of microstructure across several length scales, ranging from macro-scale porosity down to crystallographic level. At the crystallographic level, it is found that the defective nature of the microstructure is due to intergrowth from number structural variants that evolve concurrently during the thermal treatment. The structure of δ-Al_2O_3 itself is fund to be a highly complex, lacking a long-range periodicity and requiring a rationalization in terms of several closely related crystallographic variants. The two main variants are identified as δ_1-Al_2O_3 and δ_2-Al_2O_3. Full crystallographic description was obtained on the basis of quantitative analysis of HAADF STEM images from a number of low indexed zones, as shown in Fig.1(f,g) and XRD analysis. Analogous characterization effort has been performed for θ-Al_2O_3.

The validity of derived structures was evaluated with NMR measurements and DFT based modeling. It will be shown how energetic degeneracy among the various transition alumina leads to complex intergrowths. In Fig.1(h) we compare the stability of the newly derived δ_1-Al_2O_3 and δ_2-Al_2O_3 with γ-Al_2O_3, θ-Al_2O_3, and the thermodynamically stable α-Al_2O_3. In the final part of this talk, we describe the evolution of transition Al_2O_3 during thermal treatment, and discuss the mode of their phase transformations [4].

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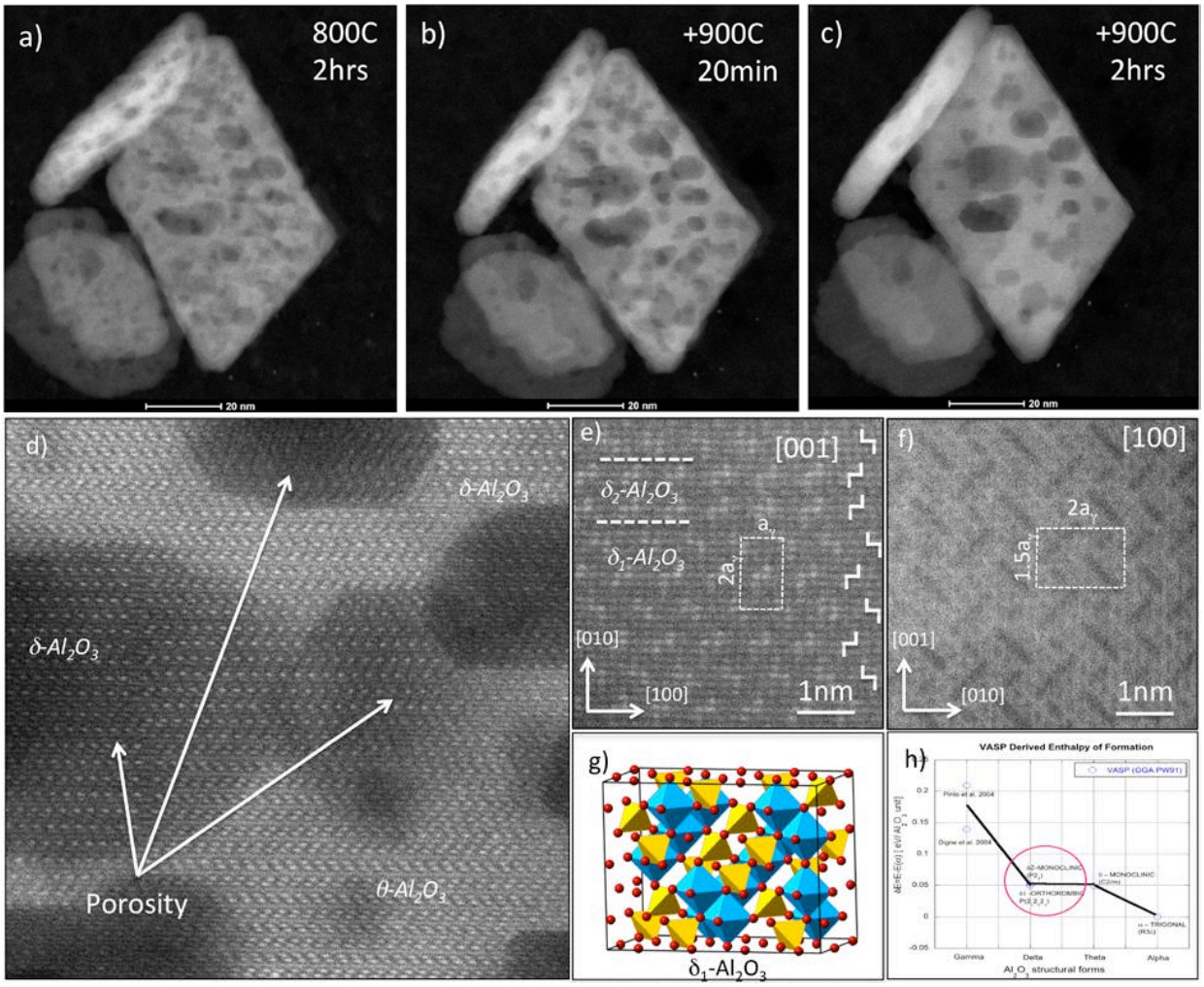

Figure 1. (a,b,c) HAADF observation of microstructural evolution of transition Al_2O_3 during in-situ heat treatment. (d) HAADF image depicting the domains of δ-Al_2O_3 and θ-Al_2O_3 in a common intergrowth (2hr@900°C), (e,f) Atomic level depiction of δ_1-Al_2O_3 along [001] and [100] crystallographic directions. (d) Schematic representation of δ_1-Al_2O_3. (e) Comparison of enthalpies of formation for the newly derived δ-Al_2O_3 and other relevant Al_2O_3 [3].

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