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Multimodal Approach for Rationalization and Quantification of Structural Disorder in Transition Al_2O_3

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Transition aluminas form a basis of important catalytic and catalytic support materials due to their unique surface acidity, high temperature structural stability, and their viability for synthesis as high surface area materials [1]. The origin of transition aluminas attractive properties has been extensively studied in the past 50+ years, but despite this effort, there are number of structural, electronic and surface properties that remain poorly understood. The poor understanding stems mostly from the inadequate crystallographic description of transition alumina polymorphs of γ-Al_2O_3, δ-Al_2O_3, θ-Al_2O_3 that evolve as a continuum of metastable structures [2,3].

This work focuses on rationalization and quantification of structural disorder in Boehmite derived transition aluminas by using a suite of complementary imaging, spectroscopy and quantum calculation techniques. Based on aberration corrected STEM HAADF imaging, it will be shown that the individual polymorphs of δ–Al_2O_3 and θ-Al_2O_3 accommodate a significant degree of structural disorder, which leads to loss of crystallographic periodicity. Figure 1(a,b,c,d) shows an example of atomic level microstructure of δ-Al_2O_3 and θ-Al_2O_3 in thermally treated transition aluminas. The complexity of this disorder can be rationalized as an atomic scale intergrowth of closely related crystallographic variants. As a part of this work, we present a crystallographic approach based on real space interpretation of projected atomic potential that enabled us to unambiguously derive Al^{3+} coordination in δ-Al_2O_3 and θ-Al_2O_3 from a series of low-index STEM HAADF images. This work lead to a full crystallographic description of the crystallographic variants belonging to δ-Al_2O_3 and θ-Al_2O_3 family, as shown in Fig.1(e,f)

To quantify the heterogeneous microstructure of transition aluminas on statistically relevant bases, we employed novel approaches for characterization of structural disorder using XRD and NMR techniques. XRD is one of the most employed methods for crystallographic bulk characterization, but historically it has not been successfully used on transition alumina. It will be shown that the crystallographic polymorphs and their structural disorder can be quantified with the use of recursive algorithms as implemented in DIFFAX and TOPAS XRD simulation packages [4]. An example of quantification of high temperature microstructure from the recursive fitting is shown in Fig.1(g). To further validate the quantification of structural disordered in transition Al_2O_3, we also employed complementary NMR spectroscopy, combined with DFT NMR simulation methods, as depicted in Fig.1(h). As a part of this talk, we also discuss results from DFT energetic calculations (Fig.1(i)) explaining how energetic degeneracy between the number of crystallographic variants leads to structural disorder in transition aluminas [5].

References:

[1] Busca, G. (2013), *Catalysis Today*, 1–12.
[2] Kovarik *et al*, (2014). *The Journal of Physical Chemistry C*, **118**(31), (2014), p.18051–18058.
[3] Kovarik, L. *et al*, *Chemistry of Materials*, **27**(20), 7042–7049. (2015)
[4] Treacy, M., Newsam, J. M., & Deem, M. W., *Proc. R. Soc. Lond. A*, **433**, 499–520, (1991)
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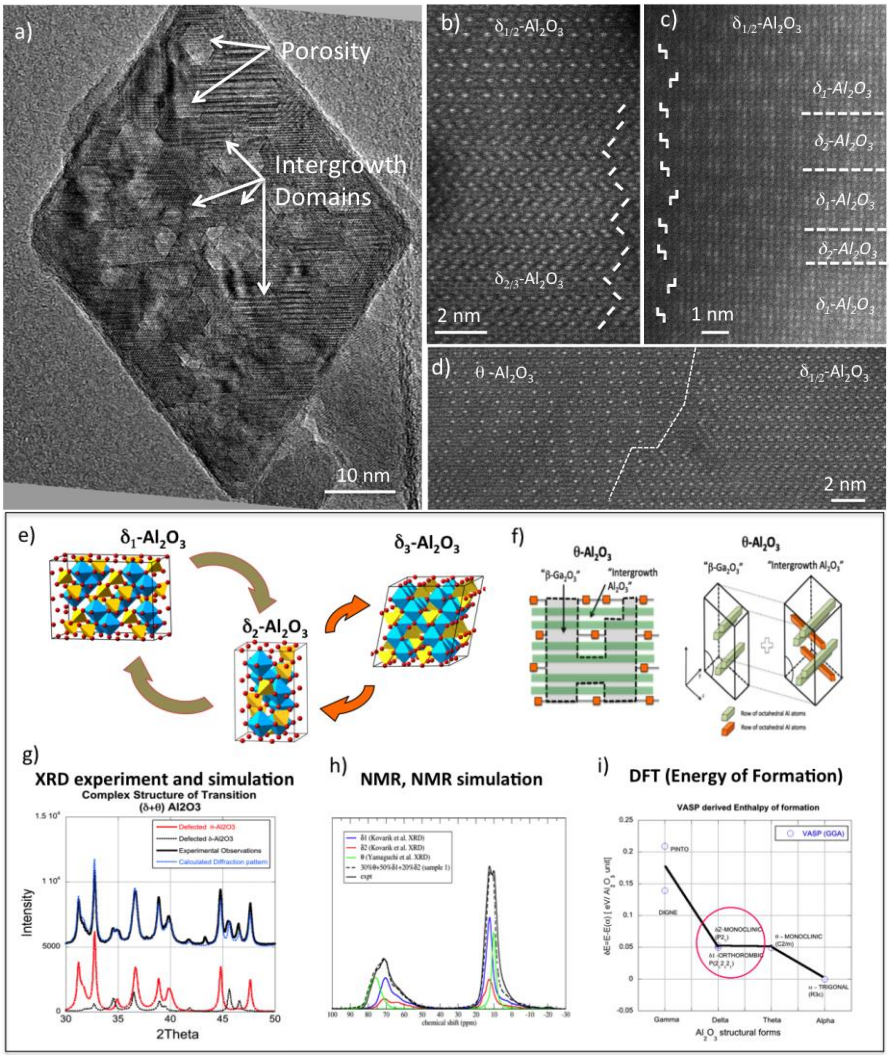

Figure 1. (a,b,c,d) TEM and HAADF observations of microstructural disorder in high temperature transition Al_2O_3 (e) Crystallographic representation of closely related δ-Al_2O_3 family variants (δ_1-Al_2O_3, δ_2-Al_2O_3, and δ_3-Al_2O_3). (f) Representation of θ–Al_2O_3 as atomic level-structural intergrowth (g,h) XRD and NMR quantification of the microstructure (i) DFT derived enthalpies of formation for δ□Al_2O_3, θ□Al_2O_3 and other Boehmite derived polymorphs of Al_2O_3.

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