Nanostructured Gamma Alumina from Amorphous Precursors

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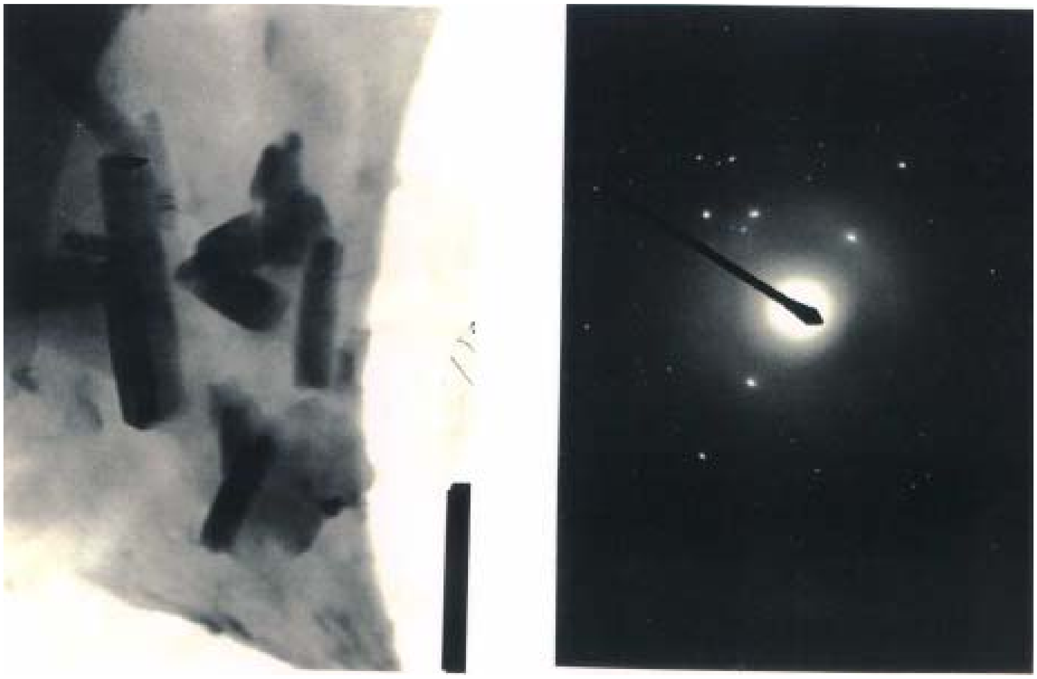
Introduction

Nanocrystalline gamma-phase (γ) alumina is among many polytypes of alumina that find extensive applications as a catalyst and catalytic supports. The most useful properties these aluminas provide as catalyst supports are high surface area and well-defined porosity. These properties result primarily from the nano-scale crystalline character of the alumina. The problem is that both the alumina precursor phase type and the thermal history have pronounced effects on the gamma structural transformations. Thus, precise control over the gamma transformation is a key to understanding many of the mysteries associated with this material in catalytic processes (1). We will clearly demonstrate that very significant atomic rearrangements take place at relatively low temperatures in the gamma-alumina amorphous precursors that affect both the gamma structure, and the ultimate transition to the thermodynamically stable alpha phase.

Results and Discussion

There is an impressive body of literature that describes the pathways of the transformations for various precursor aluminas to the alpha phase (2). However, the alpha phase is not so exciting for most catalyst studies. Focusing on the more widely used gamma phase, there remain many unresolved issues concerning its composition and defect structure. In order to investigate nano-scale structural effects, several advanced analytical and modeling techniques were utilized for this work. Included were the following: first-principles atomistic modeling of gamma-alumina stabilized with La, conventional and Z-contrast transmission electron microscopy of same, selected area electron diffraction, synchrotron EXAF spectroscopy, quantitative XRD (with calculation of structure factors and radial distribution functions to characterize the chemical and topological short-range order in alumina amorphous precursors), and thermal analysis. In addition, combinations of these very powerful techniques allowed the possibility to estimate the positions of individual atoms in the crystalline lattice of selected **γ-**aluminas.

We have found that the sometimes unusual chemistry associated with the commercial production of gamma alumina is actually a natural consequence of the fact that quite different products may be obtained depending on the atomic structure of their respective amorphous precursors and subsequent thermal treatments (e.g., in the alkoxide route of production). As an example, two **γ-**alumina samples were commercially produced by different thermal treatments to the same surface area and XRD phase type. Subsequently, both were annealed for sixteen hours at 1000°C. XRD analysis then showed phase conversion of one sample to delta/theta type and the other to predominately alpha type alumina. We can now explain differences between these apparently similar gamma products from nano-scale analyses and comparisons of their "amorphous precursors." In the photo-micrograph below, we show good evidence that the gamma product with less thermal stability (transitioned to alpha alumina after 16 hours at 1000°C), had large cigar-like crystallites dispersed in its amorphous matrix. The morphological analysis of these crystallites (i.e., the construction of thermodynamically stable crystal shapes using the Wolff-Bragg theorem) indicated that diaspore formation was quite likely. Of course, its presence in the boehmite transformation sequence needs to be further proved and analyzed from the space group sequence analysis to make sure it does not contradict the symmetry group/subgroup relationships (3). The adjoining picture of micro-diffraction features several distinctive reflections from one crystallite. The diffuse scattering from the amorphous substrate can also be easily detected.



With the development of this analytical expertise came the ability to better understand, and consequently control, how elements like lanthanum and silicon affect the gamma stabilization and transition. Understanding the mechanism of these stabilizing agents, on an atomic scale, is key to optimizing their usage in new catalysts. This subject has been the focus of much recent debate (4). We will offer evidence that the elements primarily act on free (grain) surfaces, rather than in the bulk volume obtained using first-principles atomistic calculations, the results of Z-contrast STEM studies, and synchrotron EXAFS-spectroscopy.

References

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