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Studies of Single Dopant Atoms on Nanocrystalline γ-Alumina Supports by Aberration-Corrected Z-contrast STEM and First Principles Calculations

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γ-alumina is one of metastable polytypes of Al_2O_3 that is used extensively as a catalytic support material because of its high porosity and large surface area [1]. At temperatures in the range 1000-1200ºC, however, γ-alumina transforms rapidly into the thermodynamically stable α-alumina phase (corundum), drastically reducing the surface area and thus suppressing the catalytic activity of the system [2]. The phase transformation can be shifted to higher temperatures by doping γ-alumina with one of many elements such as La, Ba, P, or Si. It has been demonstrated that as little as 0.3-0.5% La can induce stabilization of γ-alumina [3]. While a considerable amount of bulk thermodynamic data have been accumulated, no information is available on the atomic-scale mechanism of phase transformation or changes thereof introduced by dopants. In this paper we report the use of a combination of atomic resolution Z-contrast microscopy and first-principles theory to investigate the interaction between La atoms and alumina catalytic supports. This combination of tools has proven to be quite powerful for structure-properties correlation at interfaces and nanostructures [4].

Z-contrast imaging [5] is a very convenient method of revealing atomic arrangements because it allows for direct interpretation of contrast in terms of atomic positions. The fact that brightness is roughly proportional to the square of atomic number Z makes this technique uniquely suited for detection of heavy atoms on light supports. The advent of spherical aberration correction for STEM, which is expected to more than double the achievable resolution [6], greatly expands the range of accessible lattice spacings and improves signal to noise parameters of the images.

Figure 1 compares images of single La atoms on a γ-alumina support obtained with amVG Microscopes' 300 kV HB603U STEM before (a) and after (b, c) aberration correction. Although they are visible in both images, they show more contrast and a better signal to noise ratio after correction. A histogram of the full-width-half-maxima (FWHM) of intensity profiles across single La atoms (Fig. 1 (b), inset) gives the probe FWHM as about 0.7 – 0.8 Å. Line scans were taken in the vertical direction to avoid the effects of drift, which was predominantly in the horizontal direction. The smaller probe also gives a greatly improved image from the alumina itself. Although very faint lattice fringes can be discerned in the uncorrected image (arrowed), after correction, individual Al/O columns are clearly seen in Fig. 1 (c). The La atom positions are directly seen to coincide with (100) atomic columns of the spinel lattice of γ-Al_2O_3. The distribution of the dopant atoms follows no apparent pattern, suggesting that they are effectively isolated, i.e. the interaction with oxide support is stronger than that between neighboring La atoms. This picture is quite different from that discovered in a previous study of Cr-doped aluminas [7], where Cr atoms exhibited a pronounced tendency to clustering.

First-principles density-functional calculations confirm uncorrelated distribution of La atoms; the results also suggest that dopant atoms stay predominantly on the surface of the support. Efforts are currently underway to utilize the nanometer-scale depth of focus of the corrected STEM for determining the three-dimensional position of dopant atoms in

order to provide experimental support for this conjecture. Details of La atoms coordination on the surface with respect to surface orientation will also be discussed.[8]

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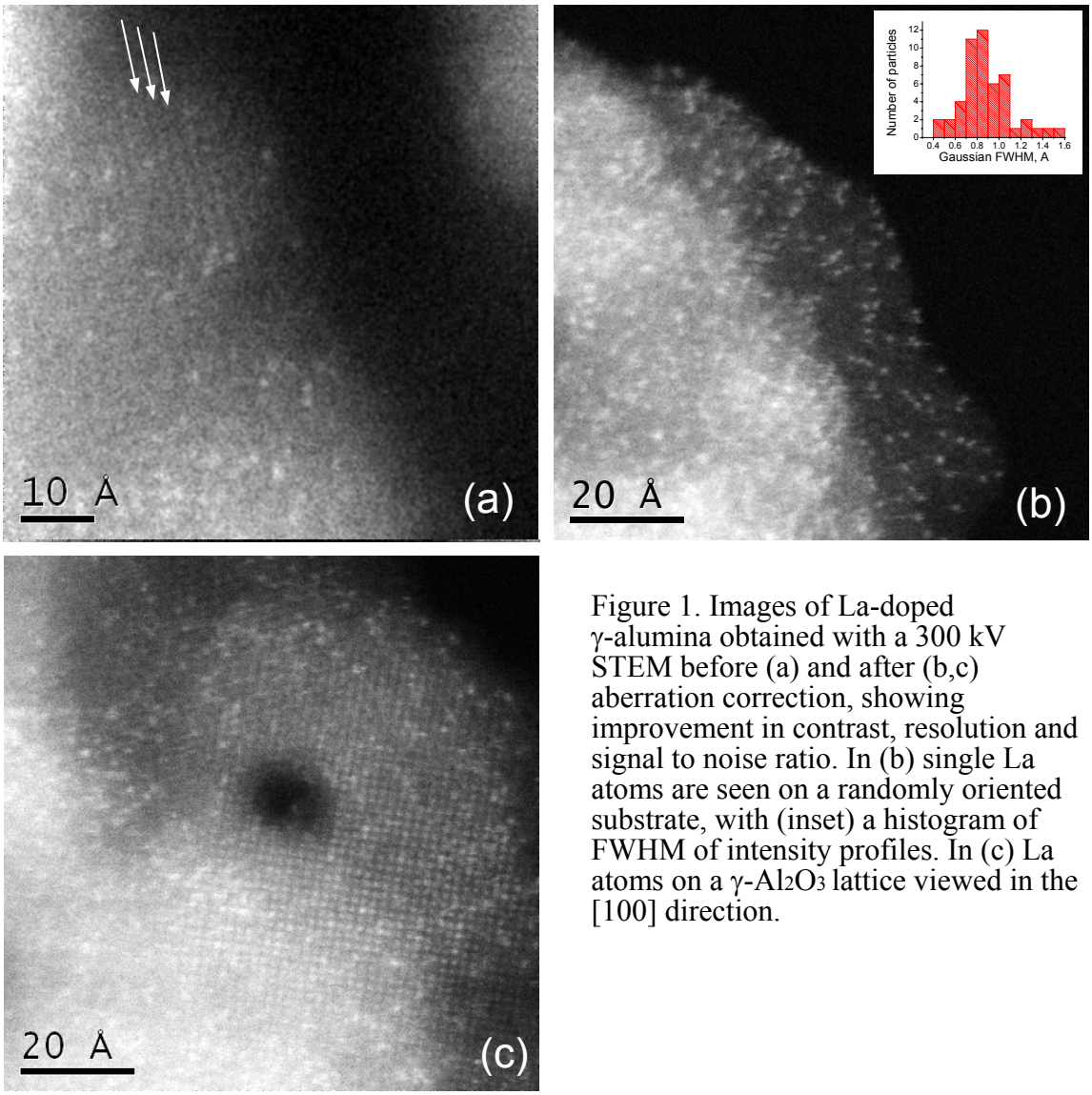

Figure 1. Images of La-doped γ-alumina obtained with a 300 kV STEM before (a) and after (b,c) aberration correction, showing improvement in contrast, resolution and signal to noise ratio. In (b) single La atoms are seen on a randomly oriented substrate, with (inset) a histogram of FWHM of intensity profiles. In (c) La atoms on a γ-Al_2O_3 lattice viewed in the [100] direction.

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