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# Ultrahigh Resolution STEM and NMR Studies of Poorly Crystalline γ–$Al_2O_3$ Surfaces: New Insights From Imaging and Spectroscopy

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γ-alumina, one of the metastable 'transition' alumina structural polymorphs, is an important catalytic material both as an active phase and as a support for other catalytically active phases, with widespread applications ranging from petroleum refining to automotive emission control. As such, the bulk and surface structure of γ-alumina, and its formation and thermal stability, have been and continue to be the subject of a considerable amount of research [1]. However, due to the low crystallinity and very fine particle size of γ-alumina, it is very difficult to apply well-established analytical techniques for determining its surface structures. Of particular importance for understanding the catalytic properties of γ-alumina, relating its surface structure to the origin of Lewis acidity has been of considerable interest and has been studied by solid state nuclear magnetic resonance (NMR) [2] and fourier transform infrared (FTIR) [3] spectroscopies, and most recently by theoretical calculations [1].

In many heterogeneous catalysts, the interaction of metal particles with their oxide support can alter the electronic properties of the metal and can play a critical role in determining particle morphology and maintaining dispersion. We have used a combination of high-angle annular dark-field scanning transmission electron microscopy and ultrahigh magnetic field, solid state magic angle spinning NMR, coupled with density functional theory calculations, to reveal the nature of anchoring sites of catalytically active phases of barium oxide and platinum on the surface of γ-$Al_2O_3$. The results obtained show that coordinatively unsaturated penta-coordinated $Al^{3+}$ ($Al^{3+}_{penta}$) centers present on the (100) facets of the γ-$Al_2O_3$ surface are anchoring sites for these catalytic phases. At low loadings, the active catalytic phase is atomically dispersed on the support surface, whereas two-("rafts") and three-dimensional structures form at higher coverages. The ability to control the dispersion, morphology and stability (typical characteristics that determine the performance of catalysts) of oxide supported metal catalysts is a primary goal of catalyst design and can be enabled by understanding the nature of metal - support surface interactions. Precious metals (e.g., Pt, Pd, Rh) supported on oxide surfaces are the most widely used industrial catalyst materials. For these classes of catalysts, dispersion of the precious metal on the oxide support is an especially critical factor, because of the expense of the metal.

Figure 1 is a high-angle annular dark-field (HA-ADF) scanning transmission electron micrograph of a 2 wt% BaO/γ-$Al_2O_3$ sample [4]. This high-resolution image clearly shows that single BaO molecules are dispersed on the surface of γ-$Al_2O_3$. This observation is consistent with the results of our high resolution $^{27}Al$ solid state NMR study that showed the preferential anchoring of BaO monomers onto penta-coordinate $Al^{3+}$ ($Al^{3+}_{penta}$) sites formed by the dehydroxylation of the γ-$Al_2O_3$(100) surface [5]. Similar results to this have been obtained for the controlled preparation of Pt catalysts [6]. In this presentation, we will compare and contrast the behavior of these two

catalytic phases with respect to their initial dispersions and stability towards deactivation via sintering. In particular, we will follow the growth and morphology of $\gamma$-$Al_2O_3$-supported catalytic structures in-situ during simulated catalyst aging [7].

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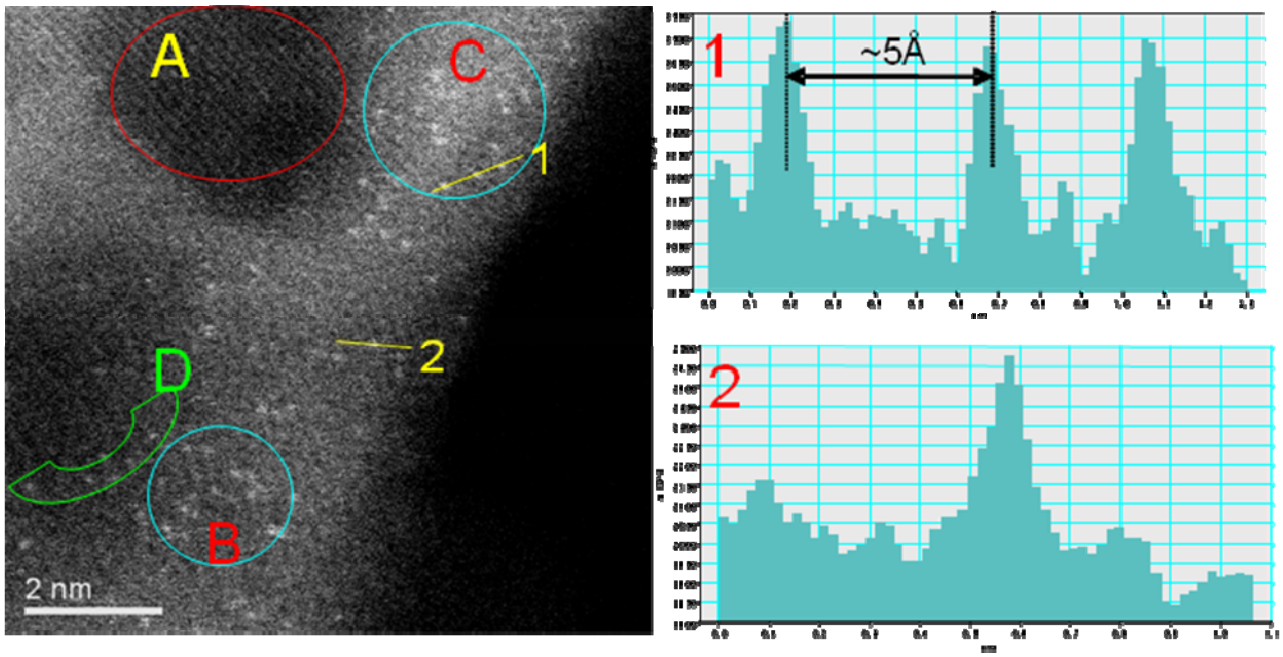


FIG. 1. HR-STEM image of a 2 wt% BaO/$\gamma$-$Al_2O_3$ sample. Normalized intensities across BaO monomers at two different regions of the image are also shown (1 and 2).

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