

Yttrium Dopants in Titania: Not Structurally Incorporated but Bound at Surfaces

Structurally incorporated impurities have been shown to have systematic effects on the rate of the thermally driven transformation in titania nanoparticles [1-4]. The anatase-to-rutile transformation is slowed when anatase nanoparticles are doped with a cation of valence $> +4$, but favored when the valence $< +4$. Based on these observations, Y^{3+} dopants should promote the anatase-to-rutile transformation. However, prior studies showed that the transformation is inhibited by Y^{3+} impurities [1,2], without explaining this observation. In a study led by the scientists of University of California Berkeley and Lawrence Berkeley National Laboratory, extended x-ray absorption fine structure (EXAFS) experiments on yttrium-doped titania nanoparticles were conducted for determining the local structural environment of Y^{3+} impurities. The experiments were developed in collaboration with SSRL beamline scientists at BL 10-2 and 11-2.

The EXAFS setup is shown in Figure 1. The measurements at the Y K-edge (17300 eV) were made up to $k = 12 \text{ \AA}^{-1}$. A Lytle detector was used with helium gas flowing through the sample chamber and Ar gas through the detector chamber. The x-ray energy was calibrated with Y foil before the experiments. For harmonics rejection the monochromator was detuned by 50%. Because the doping concentration of yttrium is relatively low, fluorescence mode was used.



Figure 1: The EXAFS experimental setup. A Si(220) crystal was used in the monochromator with an energy resolution of about 1 eV. Sample powders were brushed onto sticky Kapton tape.

The fit results (Figure 2) indicate that the Y impurity does not exist as $(Y_xTi)O_{2-3x/2}$, i.e., the Y impurity is not structurally incorporated. This differs from the cases of doping TiO_2 with some other ions (e.g. Cr^{3+} , Fe^{3+}), where impurities are distributed within the nanoparticles [2,3]. The reason why Y^{3+} does not substitute for Ti^{4+} in TiO_2 nanoparticles is very likely the difference in the size of the Y^{3+} (0.892 \AA to 1.10 \AA) and Ti^{4+} ions (0.53 \AA to 0.605 \AA) [5]. Moreover, the first shell scattering in the EXAFS data is well fitted by Y-O bonds of length $\sim 2.3 \text{ \AA}$, a nearly 20% mismatch with the Ti-O bond lengths in the nanoparticles (1.92 \AA and 1.96 \AA) [6]. For heat-treated nanoparticles, the first shell Y-O coordination number is six, consistent with the yttrium oxide (Y_2O_3) structure. However, the characteristic XRD peaks of Y_2O_3 are not detected from our samples indicating that, if present, individual clusters of this phase should be smaller than $\sim 1 \text{ nm}$. Furthermore, the Y-O bond length ($\sim 2.3 \text{ \AA}$) is larger than that of bulk Y_2O_3 (2.2749 \AA) [7]. It can be concluded that yttrium impurities are mostly present as individual, oxygen-coordinated atoms at the titania surface (i.e., as YO_6 groups) and about 15% of the surface oxygen sites are bound to Y.

Together with the observation of the structural modification and phase transformation retardation in the complementary wide-angle x-ray scattering experiments for the study, it has been found that the low concentrations of yttrium surface impurities on nano-anatase reduce surface energy and inhibit nanoparticle growth over a large temperature range. As a consequence, the anatase phase is also stabilized, as the anatase-to-rutile transformation does not occur below 700 °C. The findings demonstrate the effectiveness of surface bound impurities of stabilizing nanoparticle size and phase, an issue of great importance for retaining the materials properties of nanoscale catalysts that operate at high temperatures.

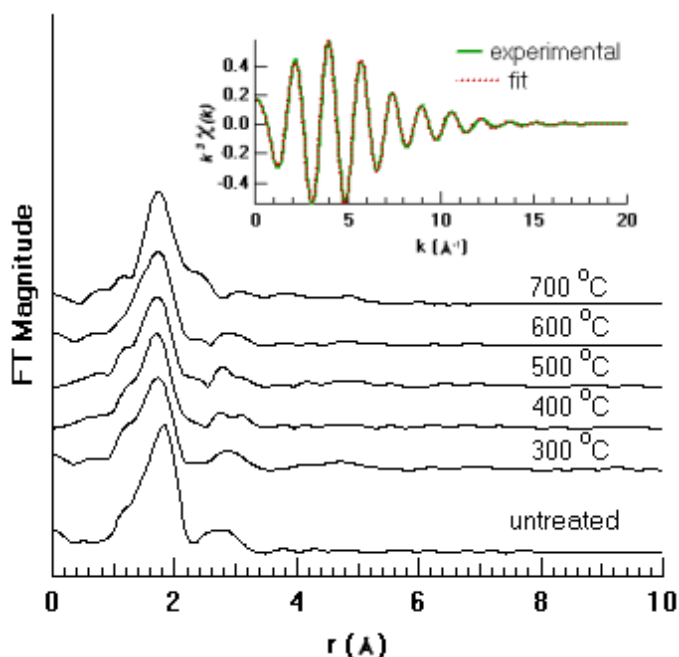


Figure 2: Fourier transform magnitude of k^3 -weighted Y K-edge EXAFS spectra of yttrium-doped TiO_2 nanoparticles as a function of treatment temperature. **Inset:** A representative one of the k^3 -weighted first-shell EXAFS spectra (solid green line) and the fit (dashed red line).

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References

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