

## **NIRT: Surface reactivity of nanocrystalline oxides and oxyhydroxides: Implications for processes in the environment**

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Nanometer-sized particles of oxides and oxyhydroxides are abundant products of chemical weathering and biomineralization. They are common in rivers, lakes, oceans, soils, sediments and atmospheric dust, where they can directly impact the bioavailability of contaminants and nutrients, the structure and properties of sediments and soils, and the dynamics of processes in the atmosphere and biosphere (1).

The properties, surface and bulk structure, and reactivity of nanoparticles are size-dependent, and cannot be determined by extrapolation of bulk characteristics. Our goal is to investigate these interrelationships in nanometer-scale oxide minerals, because these are especially relevant in the Earth's environments.

It is especially common for Fe, Al, Mn, and Ti-oxides and oxyhydroxides to occur in a surprising variety of polymorphic forms in natural finely particulate materials (2). **Our first objective** is to explore the extent to which phase stability varies with particle size. This can occur due to differences in surface energy between polymorphs. TiO<sub>2</sub> is used as a model system.

TiO<sub>2</sub> has three commonly occurring structures: rutile, anatase and brookite. Our first goal is to investigate, via direct measurement and molecular simulation, the relationships between size and nanoparticle structure. Nanocrystalline anatase, brookite, rutile, and mixtures of anatase and rutile were studied using high temperature molten oxide drop solution calorimetry at 975 K with 3Na<sub>2</sub>O•4MoO<sub>3</sub> solvent using a Calvet type twin microcalorimeter (3). The transformation enthalpies for bulk (coarse) materials (anatase-rutile and brookite-rutile) and the surface enthalpies were derived from the calorimetric data. Relative to bulk rutile, bulk brookite is  $0.71 \pm 0.38$  kJ/mol and bulk anatase is  $2.61 \pm 0.41$  kJ/mol higher in enthalpy. The surface enthalpies of rutile, brookite, and anatase are  $2.2 \pm 0.2$  J/m<sup>2</sup>,  $1.0 \pm 0.2$  J/m<sup>2</sup>, and  $0.4 \pm 0.1$  J/m<sup>2</sup> respectively (3). The closely balanced energetics directly confirm the crossover in stability of nanophase polymorphs inferred by Zhang and Banfield (4).

Molecular dynamics has been used to simulate 2 nm to 4 nm diameter nanoparticles at 300 K to further investigate effects of size and surface energy on phase stability. The potential of Matsui and Akaogi (5) for titanium dioxide was chosen, based on the analysis of Collins et al. (6), and others. The molecular dynamics software package DLPOLY was used for molecular dynamics simulations. The simulations were carried in NVT (canonical) ensembles using 0.005 ps time steps. Simulations were run for 600,000 time steps (3 ns). The system was equilibrated for 1ns before any data collection. Spherical particles conforming to a specific phase were used as starting structures. XRD patterns are determined using Debye functional analysis to monitor the structural properties. Although there is rearrangement at the surface of the particles the simulations do not undergo phase transformation at 300 K, probably because there is insufficient thermal energy to overcome the activation barrier for phase transformation.

Simulations at higher temperatures are being carried out to determine the temperature at which there is a phase transformation and the heat capacity for nanoparticles as a function of size. The heat capacity determinations and phase transformation simulations will be correlated with experimental and modeling results. We are currently simulating nanoparticles in water and

will investigate the effects of ions ( $H^+$ ,  $Cl^-$ ). The change in surface state, thus reactivity, due to the binding of ligands will be especially relevant to parallel studies.

Surface adsorption and desorption reactions on high surface area natural nanomaterials play significant roles in controlling the form and distribution of ions. **Thus, our second goal** is to understand how nanoparticle surfaces and surface reactivity change with size. We synthesize nanoparticulate anatase ranging down to  $\sim 3$  nm in diameter and use experimental surface titrations to measure surface charge. Data are interpreted using the MultiSite Complexation (MUSIC) model of Hiemstra et al. (7) extended by Machesky et al. (8) to include temperature dependence. Surface protonation constants can be estimated explicitly for the different types of surface groups present, allowing calculation of the pristine point of zero charge,  $pH_{ppzc}$ . Ultimately, the spherical form of the Poisson-Boltzmann equations will be incorporated into our MUSIC modeling because the radii of nanoparticles may be smaller than the diffuse double layer thickness. This results in the divergence of the electrostatic lines of force, with the result that the electrical double layer can adsorb more charge for a given surface potential.

First, we analyzed the surface charge of bulk rutile and anatase. Our surface titration studies using 40 nm anatase gave a very reproducible  $pH_{znpc}$  of about 6.03, comparable to previously reported values ( $\sim 5.9$  to 6.1). Predicted bulk-anatase protonation constants at 25°C, taking into consideration morphology, yield a  $pH_{znpc}$  of 6.03. The excellent match with the experimental value indicates the MUSIC Model describes the bulk anatase surface.

It has been proposed that much of the reported enhanced reactivity of nano-anatase is due to the presence of an increasingly large population of coordinatively undersaturated Ti surface sites as size decreases. After making certain assumptions about Ti-O bond lengths and coordination, we estimated the  $pH_{ppzc}$  value of 1.9 nm anatase as 3.63, much lower than for bulk-anatase. This suggests that the  $pH_{ppzc}$  of anatase decreases with decreasing particle size. However, other reasonable assumptions can be made, based on the literature, and with two alternate scenarios the estimated  $pH_{ppzc}$  values were 5.38 and 6.51. Consequently, good experimental measurements are essential.

We also obtained experimental data for 10 nm anatase and found that the  $pH_{znpc}$  is similar to that for 40 nm anatase. Any decrease in the  $pH_{znpc}$  value is anticipated only for particles  $< 10$  nm. To see the possible electrostatic effects of the convergence of particle size and EDL thickness, particles of mean diameter  $\leq$  about 6 nm and titrations in 1:1 electrolyte media of 0.01M concentrations will be necessary. Ongoing work involves analysis of  $\sim 3$  and 6 nm diameter anatase (a preliminary result of  $\sim 5.2$  was obtained). We will document the predominant crystal planes exposed via TEM so as to rationalize measured  $pH_{znpc}$  values within the MUSIC Model framework.

The fate and transport of natural nanoparticles depends strongly on nanoparticle size and aggregation state. **Thus, our third goal** is to understand how nanoparticle growth and the aggregation state are affected by size, surface charge, and solution chemistry, and how surface charge and phase stability are interconnected. We are particularly interested in the ways in which solution chemistry changes the role of oriented aggregation-based vs. Ostwald ripening-based crystal growth and how pH affects phase stability.

We conducted experiments in pH 1.9 to 12.5 solutions aqueous solutions under hydrothermal conditions using nano-sized titania (initial material is 85% anatase 15% brookite). XRD, BET, and TEM were used to characterize size, morphology, aggregate structure, and to determine phase weight percentages.

Coarsening at 200°C at pH << ZPC (preliminary nano-titania estimate is 5.2) led to rapid conversion of anatase and brookite to rutile. This is attributed to increased Oswald ripening due to increased Ti solubility below pH ~ 1.5. At pH near the ZPC, the phase content remains unchanged over time and anatase crystals grow predominantly via oriented attachment. In this regime, the largest crystals have needle-like, symmetry-breaking morphologies, possibly because initial attachment on one surface changes the probability of attachment on what would otherwise be identical surfaces. At pH >> ZPC, brookite quickly converts to anatase without rutile formation, and the size of a subset of particles increases rapidly. Even after very long coarsening times and dramatic crystal growth, the titania remains 100% anatase, although rutile is normally considered the thermodynamically stable phase at this size. This finding may indicate pH-dependent changes in surface energy modify stability crossovers. Results indicating interdependence of thermodynamic phase stability, the interfacial energy, and growth mechanism will be addressed via surface and molecular modeling.

**The final objective** of our current work is to investigate the surface reactivity of nanocrystalline anatase by studying the particle size dependence of phase transformations initiated by interface nucleation. The Johnson–Mehl–Avrami–Kolmogorov (JMAK) and other equations frequently used to describe phase transformations cannot describe nanocrystalline anatase to rutile transformation kinetics. However, the kinetics can be described using our recently developed interface nucleation model, which is supported by detailed structural analysis of the transformation mechanism. We have developed expressions that relate the number of anatase particles transformed to rutile per unit time to the square of the number of the anatase particles.

Using XRD we determined the phase transformation kinetics in nanocrystalline anatase samples with average particle sizes ranging from 8.2 to 21.4 nm, in the temperature range 480 - 580 °C (20 °C increments). The kinetic data fit the interface nucleation model fairly well. The kinetic constants increase dramatically with decreasing initial average anatase size.

We have derived expressions that show the form of the dependence of the pre-exponent factor and the activation energy of the phase transformation on initial particle size. These indicate that the activation energy for transformation of nanoparticles is higher than for the bulk. This may be related to the higher surface energy of rutile. However, the high density of particle-particle contacts and possibly new vibration modes on surfaces may favor rutile nucleation, causing the pre-exponent factor to increase dramatically with decreasing particle size. The net effect of decreasing anatase particle size is to increase the activation energy and greatly increase the pre-exponent factor so that the transformation proceeds at an increased rate.

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