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Particle size effects on transformation kinetics and phase stability in nanocrystalline TiO_2

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ABSTRACT

Kinetic studies conducted primarily between 465 and 525 °C demonstrate that the rate of the polymorphic anatase to rutile transformation increases dramatically when the reacting anatase is very finely crystalline. Coarsening of the reactant anatase and product rutile crystallites occurs simultaneously with the transformation. Kinetic behavior and quantification of transformation rate as a function of average crystallite size indicate that the increase in favorable nucleation sites is a likely cause of increase in transformation rate at small crystallite sizes. Additionally, experimental evidence supports the reversal of stabilities of anatase and rutile at small crystallite sizes. It is proposed that the reversal of stabilities is the result of rutile having a higher surface energy than the anatase phase. Data for coarsening kinetics of anatase and rutile supports the prediction that the surface energy of rutile is significantly larger than that of anatase. Thermodynamic data and theoretical estimates are used to show that a 15% greater surface energy for rutile causes the total free energy of rutile to be greater (less negative) than anatase at crystallite diameters in the few nanometer range. Given the fact that anatase and rutile structures have no polymerized octahedral fragments in common, this may be significant in determining the nature of the nucleated phase.