514c Kinetics and Size Distributions in Deaggregation of Titania Nanocolloids

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The formation of non-aggregated nanoparticles remains a challenging task, especially for particles in the lower side of the nanometer range. Although nanosized primary particles of various materials can be readily synthesized by colloidal precipitation, the final product is typically received in a highly aggregated form. Redispersion is in some cases possible through a combination of mechanical means and chemical treatment based on peptizing agents and surfactant additives. The precipitation of titania from alkoxides under large water-to-titanium ratio is such an example: it leads to the formation of ultrafine primary particles in a highly aggregated form which can subsequently be redispersed to a high degree by acid treatment (peptization). Titania is of interest to us for several reasons. It is of relevance to chemical synthesis as a catalytic material and catalyst support, and a known photocatalyst with the ability to decompose a variety of pollutants in air and in water. Its ability to use naturally occurring sunlight to attack a variety of combustion pollutants and volatile organic compounds (VOC's), suggests the possibility of low-cost, low-energy processes based on titania for maintaining a clean air and water environment. From a broader perspective, the characteristics of this alkoxide system (rapid hydrolysis and precipitation, slow de-aggregation) are shared by other transition and group IIB metals (V, Zr, Al).

We study the redispersion mechanism of heavily aggregated nanocolloidal titania with the goal to produce stable, well-dispersed nanoparticles. The hydrolysis of titanium alkoxides in excess water produces large agglomerate structures composed of ultrafine (3 to 5 nm) crystallites; these are subject to slow deagglomeration through acid treatment to obtain dispersed particles as small as 10 nm in diameter. Our hypothesis is that the dispersion of aggregated particles is determined by the competition between cluster disintegration (deaggregation) and reaggregation of the fragments. This hypothesis allows us to experimentally measure the rate of deaggregation and study the factors that affect the dispersion of aggregates.

In these experiments, we first precipitate titania in the form of highly aggregated and very turbid suspensions of nanoparticles (5-10 nm) to aggregate sizes that exceed 1 micron. These suspensions are then treated in nitric acid of varying concentration until the suspension peptizes, as indicated by the near-transparent suspensions obtained. We monitor the kinetics of deaggregation by following the evolution of the size distribution in time. We use dynamic laser light scattering to measure the average size and utilize a combination of inversion techniques that include CONTIN, exponential sampling, and bimodal method, to infer the distribution of sizes during deaggregation. These methods use alternate hypotheses to produce an estimate of the size distribution from the measured autocorrelation function. Despite the well-known ill-posed nature of the inverse problem, the combination of methodologies allow us to obtain reliable measures of the size distribution during peptization.

We find that kinetics exhibits nearly first-order kinetics to a steady state size distribution which depends on the pH. During peptization, we observe a bimodal size distribution, with one mode located in the range 10 to 20 nm, and a larger mode that is a function of time and which reaches a steady state value that is pH dependent. We interpret these results on the basis of a aggregation/deaggregation population balance model which allows us to extract the values of the aggregation and reaggregation rate constants. We propose an erosion-type mechanism in which colloidally unstable primary particles detach from aggregated clusters and test its predictions against the experimental findings.