Solvent Effects in the Deaggregation of Titania Nanoparticles

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Abstract

We report on the effect of alcohols in the acid peptization of aggregated titania nanoparticle produced from alkoxides. Peptization was studied in the presence of each one of the following alcohols: methanol, ethanol, propanol and isopropanol. We find that the final particle size is correlated to the dielectric constant of the peptizing medium. Kinetic measurements reveal that the rate of deaggregation is not affected by the presence of alcohol; however, the tendency for reaggregation of the peptized colloid increases significantly. We conclude that alcohols prevent the full redispersion of the aggregates by decreasing the colloidal stability of the suspension. This conclusion is supported by the measured zeta potential of the peptized particles, which is found to decrease when alcohol is present.

I. Introduction

The novel optical, electronic, chemical, and structural properties of materials fabricated from nanoparticle precursors have motivated a substantial research effort in the synthesis of ultrafine particles [1-5]. A common problem is that such particles are often obtained in highly aggregated form, primarily due to the difficulty in stabilizing nanometer size particles against aggregation. With some systems it is possible to reverse the effect of aggregation and redisperse the aggregates by peptization in a suitable chemical environment. A characteristic example is the formation of titania nanocolloids from the hydrolysis and polycondensation of titanium alkoxides. This reaction produces large aggregates composed of ultrafine primary particles (3 to 5 nm) which can be redispersed through acid peptization. The degree to which redispersion is achieved varies widely. The size of the peptized particles is reported in the literature to range from about 15 nm [6] to more than 100 nm [7], which implies that the degree of redispersion is highly variable depending on the experimental conditions.

In our previous studies we have shown that the degree of redispersion has a strong dependence on the type and amount of alcohol present in the peptization medium [6]. Often, alcohol is added to the reaction mixture to provide uniform mixing of the alkoxide and water, which react rapidly upon contact. Even if no alcohol is added during synthesis, some amount is unavoidably present as a product of the hydrolysis reaction. The effect of alcohols in titania precipitation is summarized in fig. 1 which shows that the final particle size increases substantially as the concentration of the alcohol is increased. This effect is stronger in isopropanol, weaker in butanol, and intermediate in propanol (only two experimental points are given for

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Fig. 1 Size of peptized aggregates as a function of the concentration of alcohol in the peptizing medium.
the butoxide/butanol system because of the limited solubility of butanol in water). This trend can be attributed to two possible effects: the alcohol may inhibit the peptization of the aggregated colloid, or/and it may enhance the reaggregation of the dispersed particles. Both mechanisms would result in larger final particles. We have recently proposed a kinetic model of peptization based on the idea that redispersion is the result of competition between the peptization of aggregated particles and the reaggregation of the peptized colloid, and have shown that the model provides a quantitative description of the peptization of titania [8]. This model allows us to measure experimentally the rate constants for peptization and reaggregation and to correlate them to the process parameters. The goal of the present study is to elucidate the mechanism by which alcohols inhibits the full peptization of titania nanocolloids by measuring the peptization and reaggregation rate constants in the presence of various low-molecular weight alcohols.

II. Experimental

Titania nanoparticles were synthesized by reaction between titanium isopropoxide and water in the presence of nitric acid. The concentration of the alkoxide was 0.23 M and the amount of acid corresponds to [H+]/[Ti] molar ratio of 0.5. A specified amount of nitric acid (J.T. Baker) was mixed with distilled water in a glass bottle and the solution was placed in a temperature controller bath maintained at 50°C. Titanium isopropoxide (supplied by Aldrich) was added dropwise as the solutions were constantly stirred at 300 RPM. Titania is formed according to the reaction

\[ \text{Ti(iPrO)}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{iPrOH} \]

The precipitation of particles is immediately manifested by the formation of a highly turbid suspension. This suspension was divided into 5 equal samples and was let to stand for five minutes. The samples were then mixed with a specified volume of an aqueous solution containing either methanol, ethanol, propanol, isopropanol, or water only (no alcohol). Within a few hours a white-blue solution was observed indicating the progress of peptization. After 6 h of continuous stirring, intermittent stirring was applied (20 s of stirring followed by 10 s of rest) to minimize shear-induced aggregation. After 10 h, the stirring was turned off and the temperature was set to 25°C. Under these conditions peptization continues for several days as indicated by the decrease of the measured particle size and by the increased transparency of the solution. All measurements and theoretical analyses in this paper are for this slow part of the process.

Particle sizes were analyzed by withdrawing samples from the peptization medium, diluting them in water, and measuring the hydrodynamic diameter by light scattering (2030AT Brookhaven model using a He-Ne laser operating at \( \lambda = 632.8 \) nm). The reported sizes represent the average of 3 measurements. Zeta potential measurements were performed in a Zeta PALSE model by Brookhaven Instruments.

III. Peptization model

Our interpretation of the peptization experiments is based on a reversible aggregation/deaggregation model. The model has been described in detail elsewhere [8] and its salient features are summarized here. The basic premise is that while deaggregation produces smaller particles (fragments) from a cluster of primary particles but the fragments are subject to reaggregation, as shown schematically in fig. 2. In this picture a “particle” is a cluster of aggregated primary particles and the size of the cluster is detemined by the competition between deaggregation and reaggregation. Steady-state is reached when the rates of the two processes are balanced. This condition defines the final size and the degree of redispersion that can be achieved. This model provides a simple interpretation of the observed final particle size without explicit reference to the mechanisms responsible for the peptization of the aggregates, and allows the calculation of the rate constants from kinetic experiments. Treating the deaggregation rate as a first-order process in the concentration of particles, the aggregation rate as second-order process, and equating the rate of the two processes we obtain the following expression for the cluster size, \( D_x \), at steady state [8]:

\[
\frac{D_x}{D_0} = \left( \frac{3C}{K_F} \right)^{1/3}
\]

where \( D_0 \) is the size of the primary particles, \( C \) is the mass concentration of titania, \( \rho \) is the material density.
where $A$ is constant. Equations (1) and (2) provide the basis for interpreting the peptization experiments. According to Eq. (2), the deaggregation rate constant can be obtained from the slope of a semilog plot of $D/D_o = 1 + A e^{-K_d t}$ versus time. Once $K_d$ is known, the aggregation rate constant, $K_a$, is calculated from Eq. (1).

IV. Results and Discussion

In our previous work [6], the alcohol was added along with all the other reactants and thus was present during precipitation as well as during peptization. To remove any possible effect of the alcohol on the size of the primary particles and the structure and cohesiveness of the precipitates, in all of the experiments reported here the alcohol was added after the precipitation of titania. This ensures that the precipitate is formed under identical conditions and that any subsequent differences are solely due to effects during peptization. The particles were prepared by reacting titanium isopropoxide and as a result, 0.92 M of isopropanol is present in all of our samples during peptization (assuming complete hydrolysis of the alkoxide). This amount is in addition to 3 M of the selected alcohol that is mixed after precipitation and is the same in all samples. The following alcohols were included in this study: methanol, ethanol, propanol and isopropanol. Butanol is not part of this list because it has limited solubility in water (approximately 0.5 M at room temperature). In addition, one sample was peptized without adding alcohol. An equivalent volume of water was added to this sample to bring the concentration of titania to the same level as that of the alcohol-containing samples. This adjustment is necessary in order to obtain the same concentration of titania in all samples (recall that according to Eq. (1) the final size is also function of the concentration of titania). Therefore, all samples contain the same concentrations of titania and acid but differ in the type of alcohol that is present.

The kinetic experiments are summarized in Fig. 3 which shows the size (hydrodynamic diameter) of the peptizing aggregates as a function of time over a period of one week. In support of our previous findings, the presence of alcohol results in larger final sizes, thus lower degree of redispersion of the aggregated nanoparticles. The alcohol effect is most pronounced at the early stages of peptization. For example, after one day of peptization the size in water/isopropanol is about 90 nm compared 30 nm in water. The difference among various alcohols decreases with peptization time but even so the final size clearly reflects the environment in which peptization took place.

The ranking of the solvents in terms of dispersion efficiency is: water $>$ methanol $>$ ethanol $>$ propanol $>$ isopropanol. The dielectric constant of the corresponding liquids at 25°C is 78.5, 32.6, 24.3, 20.1 and 18.1, for water, methanol, ethanol, propanol and isopropanol, respectively [9]. Thus, the quality of the solvent in terms of dispersion efficiency is in the order of increasing dielectric constant. This order is preserved even after the dielectric constant of the medium is adjusted for the amount of water that is present (see Table I).

From these experiments we extract the rate constants for deaggregation and reaggregation. The deaggregation rate constant was obtained by fitting Eq. (2) to the data of Fig. 3 and the solid lines in that figure represent these fits. The reaggregation $K_a$ is calculated from Eq. (1) with $d_i=1.72$ and $\rho=3.84 \text{ g/cm}^3$.
The results are shown in Fig. 4 where we plot the rate constants as a function of the dielectric constant of the solvent. The aggregation rate constant decreases significantly, by a factor of more than 2, as we go from the low-dielectric constant solvent (isopropanol/water) to the high-dielectric constant solvent (water). By contrast, the deaggregation rate constant remains unaffected.

The correlation between rate of aggregation and dielectric constant is strong evidence that the observed behavior is due to reduced colloidal stability. To explore this hypothesis we performed measurements of the zeta potential of the peptized particles and the results are reported in Table 1. The measured potential follows the same trend as the aggregation rate constant, namely, it decreases with decreasing dielectric constant of the solvent. The decrease of the surface potential is analogous to that observed in other colloids and is attributed to the adsorption of the alcohol on the oxide surface and the subsequent reduction in the number of the ionized surface sites [10,11]. Both the zeta potential and the dielectric constant of the medium are important for stability against aggregation. In a simplified picture, the stability factor, \( W \), of the suspension can be expressed as [12]

\[
W = \exp\left(\frac{V_{\text{max}}}{k_B T} / \kappa R\right)
\]

where \( V_{\text{max}} \) is the maximum repulsive potential, approximately equal to the electrostatic repulsion between the zeta potentials of two particles,

\[
V_{\text{max}} = 2\pi \varepsilon_0 \psi_c^2 R
\]

In the above, \( \kappa \) is the inverse screening length, \( T \) is the temperature, \( k_B \) is Boltzmann's constant, \( \varepsilon \) is the dielectric constant of the solvent, \( \varepsilon_0 \) is the permittivity of free space, \( R \) is the particle radius and \( \psi_c \) is the zeta potential. In the presence of alcohols the zeta potential is found to be lower by as much as a factor of 2.5, resulting in poor colloidal stability. In addition, the decrease of the dielectric constant of the solvent further decreases the stability through Eq. (4) and also through the inverse screening length, \( \kappa \), which scales as \( \frac{1}{\sqrt{\varepsilon}} \) [12]. Even though the rate of deaggregation is not affected by the alcohol, the colloidal fragments produced by peptization are insufficiently stabilized and their reaggregation explains the larger sizes observed.

A correlation between alcohol (amount and type) and final particle size has been reported in other related oxide systems as well. Moon and coworkers synthesized monodisperse, spherical zirconia powders by the thermal hydrolysis of \( \text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} \) in an alcohol/water solution [13]. These authors showed that the presence of alcohols greatly influences the morphology and the size of final zirconia particles. Particles obtained in ethanol/water solution have soft aggregates made of ultrafine primary particles. In case of the tert-BuOH/water solution, the particles were large and spherical with a broad size distribution whereas the particles obtained from propanol/water and isopropanol/water solutions were small and spherical with a narrow size distribution. Similar observations were reported for titania synthesized under low water-to-titanium ratios [10,14,15] and for silica precipitated from alkoxides [16,17]. In all of these systems, spherical, or almost spherical, particles grow by accretion of precursor units—oligomers or small particles—to final sizes considerably larger than the ones obtained in the present study. Despite differences between these systems and the peptizing environment of our study, our results provide direct evidence that the rate of aggregation is indeed higher in the presence of alcohols and that the size increase...
can be attributed entirely to colloidal destabilization brought about by the alcohol. A second important finding of this study is that alcohols have no effect in the deaggregation process itself, as demonstrated by the constant value of $K_d$ in all samples. Therefore, neither the type nor the amount of alcohol interferes with the breakage of aggregates. This result supports the notion that the mechanism of deaggregation is not electrostatic but rather chemical in nature, involving the breakage of chemical bonds between adjacent primary particles [8].

V. Conclusions

The degree of redispersion of titania precipitates formed by the aggregation of nanometer-size primary particles is affected by the presence of alcohols in the peptizing solution. Alcohols hinder the dispersion of the aggregated particles and result in larger particle sizes. This effect can be attributed entirely on the reduced colloidal stability of the suspension which enhances the reaggregation of the peptized aggregates. The peptization mechanism itself is not affected by the presence of the alcohol and its rate constant remains the same regardless of the amount or type of alcohol present.

Acknowledgements

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Author's short biography

Danijela Vorkapic

Danijela Vorkapic was born in Yugoslavia and received her B.S. degree in chemical engineering from the University of Belgrade. During her undergraduate studies she joined North Carolina State University, Department of Material Science, for three months and worked as an undergraduate research assistant while helping design and conduct experiments on the atomic layer epitaxy of Si, SiC, and GaN. After receiving her B.S. degree, she worked in “Duga”, a paints and varnishes company in Belgrade, as a junior engineer of process development optimizing processes of coatings technology. Later, she joined Penn State University to pursue her Ph.D. under the guidance of Dr. Themis Matsoukas. For her Ph.D. dissertation she conducted studies on the kinetics and colloidal stability of nanosize titania formation for the qualitative and quantitative understanding of process mechanisms. After completing her Ph.D. she joined Air Products and Chemicals Inc where she is now a senior research engineer.

Themis Matsoukas

Themis Matsoukas received his undergraduate degree in Chemical Engineering from the National Technical University in Athens, Greece, and his Ph.D. from the University of Michigan. He was a postdoctoral researcher at UCLA and later joined the Pennsylvania State University where he is now Associate Professor of Chemical Engineering. He has conducted experimental and theoretical research in particulate systems, including synthesis and characterization of nanocolloids, modeling of particle growth in liquid and gas-phase media, the sol-gel synthesis of silica and titania colloids and gels, numerical methods for the solution of population balances, and the plasma processing of particulate materials.