THE GROWTH KINETICS OF METAL OXIDE NANOPARTICLES

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INTRODUCTION

In order to tailor the optical, electrical, chemical, and magnetic properties of nanoparticles for specific applications, it is essential to develop a fundamental understanding of the nucleation and growth processes. Metal oxide nanoparticles are usually prepared using sol-gel or precipitation methods, and particle growth can occur by aggregation or coarsening. The kinetics of these processes are strongly dependent on experimental parameters. In this paper, we discuss the growth kinetics of ZnO and TiO_2 nanoparticles from homogeneous solution as a function of the precursor, solution chemistry, and temperature.

RESULTS AND DISCUSSION

Particle growth from solution by coarsening involves the growth of larger crystals at the expense of smaller crystals, and is governed by capillary effects. Since the chemical potential of a particle increases with decreasing particle size, the equilibrium solute concentration for a small particle is much higher than for a large particle, as described by the Gibbs-Thompson equation. The growth law for coarsening was derived by Lifshitz, Slyozov and Wagner (LSW). The average radius $\bar{r}$ corrected for the average initial particle size $\bar{r}_0$ is proportional to time:

$$\bar{r}^3 - \bar{r}_0^3 = kt \quad \text{with} \quad k = \frac{8\gamma V_m^2 c_{r=\infty}}{54\pi\eta a N_A}$$

where γ is the surface energy, V_m is the molar volume, $c_{r=\infty}$ is the equilibrium concentration at a flat surface (i.e. the bulk solubility), η is the viscosity of the solvent, a is the solvated ion radius, and N_A is Avogadro's number.

Figure 1 shows the time dependence of the average particle radius obtained from the absorption onset for the synthesis of ZnO from $Zn(Ac)_2$ at different temperatures. Figure 2 shows growth data for the growth of anatase particles in water (pH 1) from titanium isopropoxide, illustrating that for anatase particles coarsening is the dominant growth mode. Figure 3 shows the results from Figure 1 re-plotted as r^3 versus time for growth at 55 ˚C illustrating that the kinetics also follow the LSW model for coarsening. The curves for growth of ZnO from $Zn(ClO_4)_2$ and $ZnBr_2$ at the same temperature illustrate the significant influence of the anion. Figure 4 shows the temperature dependence of the rate constant k for the growth of ZnO and TiO_2. It can be concluded that the materials properties and the preparation chemistry significantly affect the growth kinetics.

ACKNOWLEDGEMENT

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FIGURES

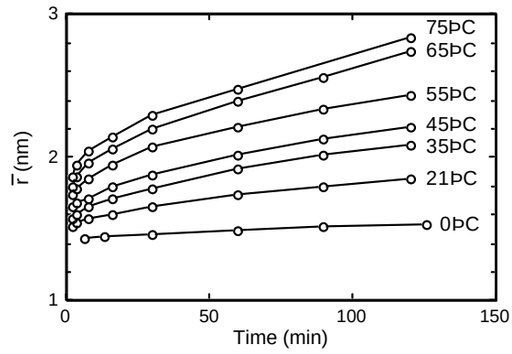

Figure 1: Average ZnO particle radius as a function of time and temperature. The particles were prepared from $Zn(Ac)_2$ in isopropanol by reaction with NaOH.

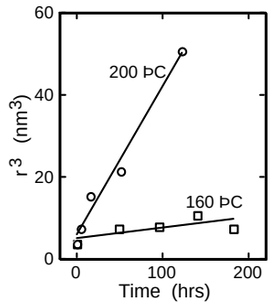

Figure 2: Average TiO_2 particle size cubed determined from TEM versus time at the indicated temperatures.

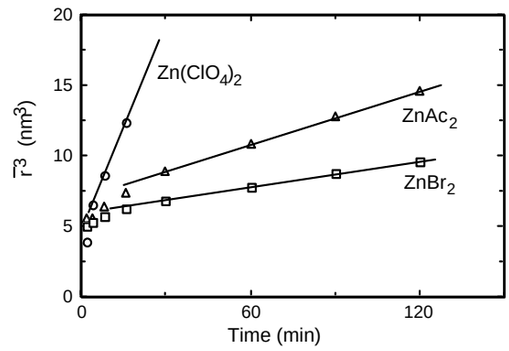

Figure 3: Average particle radius cubed versus time at 55 ˚C for 3 anions. It can be seen that the growth kinetics are strongly dependent on the precursor chemistry.

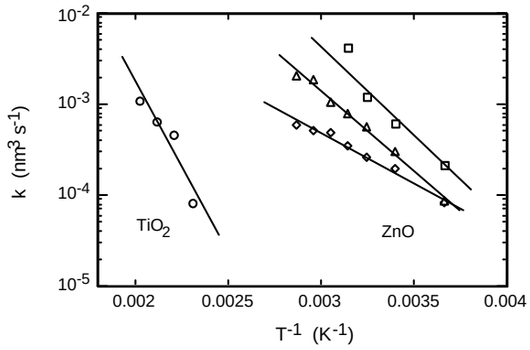

Figure 4: The rate constant for growth of ZnO and anatase (o) particles as a function of temperature. For the ZnO particles the dependence on the anion is illustrated: $ZnBr_2$ (◊), $Zn(Ac)_2$ (Δ),$Zn(ClO_4)_2$ (□)