

142ao The Kinetics and Mechanism of Rapid Nickel Oxalate Thermal Decomposition

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The global kinetics for the thermal decomposition of nickel oxalate within an aerosol flow reactor are studied by applying a one-dimensional particle phase model to the reactor. The particle velocity and axial temperature profiles are generated by the model. Because of the high heating rates attainable in an aerosol flow reactor, rapid reaction is possible. Particle residence times for the kinetic study range from 2 – 6 seconds for reactor temperatures of 695 – 767 K. The model that best fits the experimental conversion data is the first order expression. This kinetic result is interpreted as instantaneous nucleation of product nickel followed by two-dimensional growth of these nuclei controlled by diffusion of the product carbon dioxide. The best fit Arrhenius rate parameters along with 95% joint confidence interval limits are a pre-exponential factor of $1.25 \times 10^9 \pm 0.73 \times 10^9 \text{ s}^{-1}$ and an activation energy of $1.30 \times 10^5 \pm 0.20 \times 10^4 \text{ J/mol}$. As the decomposition process begins, nickel primary particles, or grains, are nucleated within the particle and continue to grow. Specific surface area increases as the reaction initiates occurs due to grain breakup resulting from increased lattice strains imposed by the vacating gaseous carbon dioxide gas. As the reaction rate slows, grain coalescence results in specific surface area reduction. A model describing the internal morphological changes that occur within the particle during the thermal decomposition process is developed. Grain boundary self-diffusion of nickel is the likely sintering mechanism. When nickel oxalate dihydrate is used as the solid feed precursor, the pre-exponential self-diffusion coefficient is $1.3 \times 10^{-9} \pm 1.2 \times 10^{-9} \text{ m}^2/\text{s}$ and the self-diffusion activation energy is $1.2 \times 10^5 \pm 6.9 \times 10^4 \text{ J/mol}$. The reported uncertainties are the 95% joint confidence intervals. Similar values are found when (dried) nickel oxalate is used as the solid precursor.