Modelling the combustion synthesis of Titania nanoparticles.

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The combustion of $TiCl_4$ to synthesize titanium dioxide nanoparticles is a multi-million tonne per year industrial process. The size and shape of these particles affects properties important to both the industrial processing and the final product, such as ease of milling and opacity of the powder. Although used in industry for decades, the understanding of the process is poor and experimental optimization is incremental and costly. As such, the ability to simulate a multi-variate distribution (for example mass, surface area, amount of agglomeration) of a population of nanoparticles created in this process is important.

We propose to present work towards a model spanning processes on all length and time scales from the molecular up to the industrial plant level. A previously published TiO_2 particle model including particle inception, surface growth, coagulation, and sintering, was based on approximate one-step chemistry[1]. Using an operator splitting method we have coupled a stochastic particle model with solvers for detailed gas phase and surface chemistry mechanisms to solve a 2-dimensional (surface-volume) population balance. This generalized model has been successfully used with existing chemistry mechanisms for the detailed simulation of soot formation in flames. The aim is to use the generalized model together with new chemistry, described below, to model the entire TiO_2 synthesis process.

Due to a lack of thermochemical data for intermediate species, it has been impossible until now to simulate in detail the gas phase kinetic mechanism. Previous simulations have used a simple overall rate expression extrapolated from experimental observations at lower temperatures. Using density functional theory (DFT) quantum calculations to find necessary thermochemical data, and estimates of the rate expressions for elementary reactions, we have developed a kinetic mechanism for the gas phase chemical reactions. Our current mechanism includes 51 elementary reactions and leads up to the formation of $Ti_2O_xCl_y$ dimer species we believe is the route towards TiO_2 nanoparticles. We shall continue this work to improve our rate estimates and extend the mechanism towards the stage where it can be coupled to the particle model.

Work is also underway to develop a mechanism for surface reactions to be included in the simulation. The growth of a TiO_2 (110) surface which is exposed to titanium tetrachloride and oxygen was studied by means of plane-wave density functional theory calculations. The activation energies of surface reactions and surface diffusion were calculated by locating their transition states on the potential energy surface (PES) using a combined linear/quadratic synchronous transit method with conjugate gradient refinements. Although a complete surface chemistry mechanism is still a long way off, we believe work in this direction will improve understanding of the surface growth of TiO_2 nanoparticles.

The aim is to produce a combined population balance model, coupling new gas phase and surface chemistry mechanisms to a particle model incorporating inception, coagulation, growth, and sintering, which can be used to simulate a plug flow reactor close to experimental or industrial conditions. This would enable a parameter investigation to find the effect changes in parameters such as temperature and pressure have on the 2D (surface-volume) population balance. We present work towards three aspects of this multi-scale problem: gas phase chemistry, surface chemistry, and solving a 2D population balance problem coupled to detailed chemical mechanisms.

[1] Neal Morgan, Clive Wells, Markus Kraft, and Wolfgang Wagner (2005). Modelling nanoparticle dynamics: coagulation, sintering, particle inception and surface growth, *Combustion Theory and Modelling*, **9**(3): 449-461