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Global sensitivity analysis of a model for silicon nanoparticle synthesis

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ABSTRACT

This paper presents a global sensitivity analysis of the detailed population balance model for silicon nanoparticle synthesis of Menz & Kraft [2013a, A new model for silicon nanoparticle synthesis, *Combustion & Flame*, **160**:947–958]. The model consists of a gas-phase kinetic model, fully coupled with a particle population balance. The sensitivity of the model to its seven adjusted parameters was analysed in this work using a High Dimensional Model Representation (HDMR). An algorithm is implemented to generate response surface polynomials with automatically selected order based on their coefficient of determination. A response surface is generated for 19 different experimental cases across a range of process conditions and reactor configurations. This enables the sensitivity of individual experiments to certain parameters to be assessed. The HDMR reveals that particle size was most sensitive to the heterogeneous growth process, while the particle size distribution width is also strongly dependent on the rate of nucleation.

1. Introduction

Knowledge of the properties of silicon has underpinned the revolution of information technology. A great deal of study has therefore been undertaken into its synthesis, purification and resultant properties. Silicon nanoparticles were first made in the late 1970s (Murthy et al., 1976) and since then, have been the subject of considerable work towards improving their manufacture and identifying potential applications.

Gas-phase, laser and plasma synthesis of particles are the most common methods with which silicon nanoparticles are manufactured (Mangolini et al., 2013). In general, these processes begin with silane (SiH_4), which may be decomposed by thermal, laser or microwave radiation (Cannon et al., 1982; Knipping et al., 2004; Nguyen & Flagan, 1991). The decomposition of silane forms reactive silicon hydrides, which combine with each other to nucleate into silicon nanoparticles (Swihart & Girshick, 1999).

Various models—from gas-phase kinetic to particle population balances—have been proposed to describe the formation of nanoparticles from silane (Menz et al., 2012; Onischuk et al., 2000; Swihart & Girshick, 1999). In all of these models, it is common to find model parameters which have uncertain values. Examples include empirical expressions for sintering (Chen et al., 2013; Menz et al., 2012; Shekar et al., 2012).

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In some cases, it is possible to estimate these values by trial-and-error (Körmer et al., 2010). However, for a non-linear model with many unknown parameters, this process becomes difficult. Systematic parameter estimation can be used to move from by-hand guesswork to computer-based solutions. For example, a model implemented in Excel® could use the GOALSEEK or SOLVER functionality to arrive at better input parameter values.

There are a range of optimisation techniques which can be used to improve model values (Kraft & Mosbach, 2010). Low-discrepancy sampling can be used to evaluate the model response over a space of parameter values (Braumann et al., 2011). Gradient-search methods such as the simultaneous perturbation stochastic approximation (SPSA) algorithm can locate local and global minima (Chen et al., 2013; Menz et al., 2012). Response surfaces, or surrogate models, can also be generated from low-discrepancy sampling, yielding a computationally efficient approximations of the true model (Kastner et al., 2013). Then, Markov Chain Monte Carlo (MCMC) sampling and Bayesian analyses are often applied to assess the credible regions in which the optimal parameter values may lie (Kastner et al., 2013; Mosbach et al., 2012).

Recently, a detailed model for silicon nanoparticle synthesis was presented (Menz & Kraft, 2013a). The model incorporates a gas-phase kinetic model, fully coupled with a particle population balance. In its original development, systematic parameter estimation was used to optimise the model's seven parameters with respect to experimental data across a range of different process conditions. However, the relative importance of each parameter in the objective function was not quantitatively addressed in this work. Nor was the influence of particular experiments on the objective function. These open questions should be addressed in order to further assess the physical relevance of the model as well as its sensitivity to input parameters.

Due to the variety of solution methods for population balance models, there are a range of different approaches for studying the sensitivity of the model's parameters. Vikhansky & Kraft (2004, 2006) demonstrated use of a gradient search method to assess the sensitivity of stochastic (Monte Carlo) solution methodologies as applied to population balance equations. In complex models, a simple scan of the parameter space can also be used (Lavvas et al., 2011; Shekar et al., 2012). An excellent review of sensitivity analysis methods is given by Tomlin (2013).

Of these methods, the high dimensional model representation (HDMR) is one which is yet to be applied to population balance modelling. In creating a HDMR of a model, one obtains a response surface for each of the supporting experiments of the model. While potentially useful for a low-computational effort optimisation, the surfaces serve a dual purpose: their coefficients reveal the model response's sensitivity to its input parameters. This information can then be used to refine the model or gain further insight into the factors which most strongly drive the results. HDMR has further benefits over conventional brute-force approaches for sensitivity analysis, as it averages over many points—this reduces the method's sensitivity to local variations in gradient (Azadi et al., 2014).

The purpose of this work is to investigate the estimated parameters in the model of Menz & Kraft (2013a) for silicon nanoparticle synthesis. A global sensitivity analysis will be conducted using HDMR response surfaces in order to elucidate the influence of each parameter in the optimisation. This will illustrate an alternative approach through which sensitivity analyses can be conducted, not as yet used in this community. Finally, the sensitivity analysis will also be applied to gain additional physical insight into the model.

The structure of this paper is as follows. A brief description of the model is given in Section 2, including the gas-phase (Section 2.1) and the population balance (Section 2.2). The techniques used for parameter estimation and sensitivity analysis are presented in Section 3. The results from the sensitivity analysis are given and discussed in Section 4.

2. Model

The model for silicon nanoparticle synthesis is composed of a gas-phase kinetic model and a particle population balance model. A full formulation of the model is given in Menz & Kraft (2013a), however, a brief description is given here. In the original development of the model, parameter estimation was used to optimise gas-phase and particle-phase parameters with respect to experimental results from the literature. This process is illustrated in Fig. 1.

2.1. Gas-phase model

The bulk decomposition of silane can be described as the bimolecular expression (Petersen & Crofton, 2003):

$$SiH_4 + M \rightarrow SiH_2 + H_2 + M \tag{1}$$

where M is a third body. It is well-understood that silane decomposition proceeds through a series of intermediate gas-phase species, such as silylene (SiH_2) and higher silenes/silanes. For this model, the mechanism of Ho et al. (1994) is adopted. The mechanism has eight core reactions, mostly described by Lindemann falloff expressions. Pre-exponential factors for five of the reactions were adjusted from their initial values. The equations describing the rate of change of chemical species due to these reactions are solved using a conventional ordinary differential equation (ODE) solver.