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On the role of gas-phase and surface chemistry in the production of titania nanoparticles in turbulent flames

Maulik Mehta [a], Venkat Raman [b], Rodney O. Fox [a],*

[a] Department of Chemical and Biological Engineering, Iowa State University, Ames, IA 50011-2230, USA
[b] Department of Aerospace Engineering and Engineering Mechanics, The University of Texas, Austin, TX 78712-0235, USA

HIGHLIGHTS

- Bivariate population balance model for titania production in flame reactors developed.
- Effect of both gas and surface phase chemistry on product particle studied.
- Flow field modeled by multi-environment plug-flow model for two experimental flames.
- Results show the importance of location of nucleation.
- Detailed gas and surface phase chemistry more accurate in description of products.

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ABSTRACT

Combustion-based synthesis is the prominent technique for large-scale production of commercial-grade nanoparticles, such as titanium dioxide (titania or TiO_2). Both time and economic constraints have led to an increase in the sophistication of the models for such chemical processes. State-of-the-art models for combustion-based nanoparticle synthesis incorporate highly detailed gas-phase kinetic models to describe the effects of the complex chemical reactions on particle formation and growth. Accurate models for particle evolution must be coupled with the detailed gas-phase kinetics in order to predict the particle properties. In this work, a bivariate population balance model for titania nanoparticle produced in flame reactors is used to investigate the role of gas-phase and surface chemistry in the determination of particle properties. The model considers all relevant particle evolution events including nucleation, surface growth, aggregation and sintering. In order to focus on the relative importance of the gas-phase mechanism, the flow field is modeled using a simple multi-environment plug-flow reactor model. Both one-step and detailed chemistry for Ti oxidation from the precursor, $TiCl_4$, are compared for two different flame configurations. The simulation results demonstrate the importance of the location of nuclei formation in the flame, which depends strongly on the gas-phase and surface growth kinetic models, and their effect on the final product properties. These results suggest that detailed gas-phase chemical kinetics combined with a detailed surface growth model are required to accurately describe the combustion-based synthesis of nanoparticles.

1. Introduction

The relevance of nanoparticles in diverse fields, such as fuel cells, drug delivery, electronics, catalysis, and coatings, has resulted in a growing interest in their bulk production. Flame synthesis represents a viable technique for large-scale production of valuable inorganic nanoparticles such as titanium dioxide (TiO_2 or titania). Nanoscale titanium dioxide have a much greater surface area for a given mass or volume of nanoparticles compared to an equivalent mass or volume of conventional TiO_2 particles. This leads to increased potential for properties such as refraction, catalysis and UV absorption. These properties have led to the exploitation of nano-TiO_2 for a wide variety of applications, including self-cleaning surface coatings, UV-resistant coatings and paints, solar cells, disinfectant sprays, and water treatment agents and topical sunscreens. Market revenues for titanium dioxide nanopowders in 2009 were US $360 million and are expected to rise up to US $1465 million in annual revenues by 2017 (Future Markets Inc., 2010).

The accurate modeling of combustion-based systems requires a comprehensive mechanism that captures the complex gas-phase chemical reactions leading to the production of the particles. This

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* Corresponding author. Tel.: +1 515 294 9104; fax: +1 515 294 2689.
E-mail address: rofox@iastate.edu (R.O. Fox).

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mechanism should precisely capture nanoparticle oxidation, as well as all of the hydrocarbon oxidation reactions taking place in the flame. Also needed is a correct description of the transition from the gas-phase species to the particulate phase and of further particle evolution (i.e., nucleation and surface growth). In flame synthesis, both fuel and nanoparticle precursor are sprayed into a pre-existing flame. The fuel evaporates and combusts, exposing the precursor to the high-temperature flame. Here, the chemical reaction mechanisms and particle growth mechanisms take over, leading to nucleation, growth and further evolution of nanoparticles. The production of these nanoparticles is tightly coupled to turbulent flames, with different size nanoparticles being obtained for different flame configurations (Pratsinis et al., 1996). The prediction of particle properties in a flame reactor is complex, involving chemical reactions, particle growth mechanism and flame dynamics. Hence, a computational model for nanoparticle production needs to provide not only accurate expressions for the aforementioned processes, but also describe the interaction between them.

The production of titania occurs through the chloride process in which the precursor, titanium tetrachloride ($TiCl_4$) is oxidized in a flame to form TiO_2 particles. Despite its commercial appeal, the kinetics of titania formation are not widely studied in the literature and most of the modeling work has been done with a global rate based on a one-step Ti oxidation reaction (Pratsinis and Spicer, 1998; Spicer et al., 2002; Tsantilis and Pratsinis, 2004; Morgan et al., 2006; Heine and Pratsinis, 2007a,b). The one-step model does not consider any Ti intermediates and thus, ignores the role that intermediates could play in the gas-phase synthesis of nanoparticles. For a more detailed look at Ti oxidation, West et al. (2009) have proposed a detailed mechanism containing 30 species and 66 reactions. Even though the major purpose of the flame is to provide energy for TiO_2 formation, its presence complicates the already complex Ti oxidation chemistry. Fuel combustion is essentially a hydrocarbon oxidation reaction and this leads to competition between the fuel and the precursor for the oxygen present. Hence, the use of a comprehensive chemical mechanism would also lead to the accurate representation of interactions between the fuel and precursor. Prior modeling work (Mehta et al., 2010) considering only the particle size has demonstrated the importance of gas-phase kinetics in predicting the properties of the final particle size distribution.

The evolution of the particle volume and surface area in the flame reactor can be tracked through a bivariate population balance equation (PBE), which models the evolution of particles undergoing processes such as nucleation, surface growth, aggregation, and sintering. In the production of nanoparticles, it is found that reactants pass through different zones where only certain source terms of the population balance are dominant (Diemer and Olson, 2005). Initially, mixing and kinetics are very important, which leads to the consumption of the precursor. Precursor consumption leads to the introduction of particles in the system and both the nucleation and growth term account for this increase in particle mass. After the precursor is consumed the evolution of product particles is generally governed by aggregation and sintering (i.e., loss of surface area at constant volume). Hence, the relative position in the flame where these particle evolution events occur determine the effect each event will have on the product properties.

In our previous work (Mehta et al., 2010), it was found that the different Ti-oxidation mechanisms (one-step vs. detailed) led to very different locations for the maximum nucleation rate. In this work, the previous findings are expanded further with the help of a bivariate population balance model involving all particle evolution events. The resulting bivariate PBE is solved using the conditional quadrature method of moments (CQMOM) (Cheng and Fox, 2010). This full population balance model is then applied to two different flame configurations, based on experimental work done by Pratsinis et al. (1996), studying both the one-step and detailed kinetics for Ti oxidation. In order to focus on the role of the chemical mechanism, the flames are modeled using a simple multi-environment plug flow reactor (PFR) (Fox, 2003), and product properties involving volume and surface area for each flame configuration using different chemical kinetics are compared. Using simple flow configurations enables the comparison of different chemical mechanisms and can help us develop and test different source terms that describe how gas-phase mechanisms affect the particle evolution. In particular, we intend to study the effects of precursor decomposition, nucleation and surface reactions on the particle evolution processes, providing a better understanding of the coupling between the chemistry and particle formation.

By using experimental data from two flames (Pratsinis et al., 1996), we can compare the relative merits of both gas-phase and surface chemistry for one-step versus the detailed mechanism in describing the particle evolution profiles. Such a detailed comparison between the chemical mechanisms would not be possible with computational fluid dynamics (CFD) simulations because of the prohibitive cost of using the comprehensive chemical mechanism coupled with turbulent flows. Thus, the principal objective of this work is to determine what level of chemistry modeling will be needed for future CFD simulations, and thus whether work to develop a computationally tractable version of the comprehensive chemical mechanism is warranted.

The remainder of this paper are organized as follows. In Section 2 we provide a brief overview of the kinetic mechanisms used to model the gas-phase chemistry of both fuel and precursor. In Section 3 we describe how the bivariate population model is set and solved using CQMOM. In Section 4 the simple flow model that is used to describe the nonpremixed turbulent mixing is presented. The simulation results for the two flame configurations and the role of surface reactions are discussed in Section 5. Finally, conclusions are drawn in Section 6.

2. Chemical mechanisms

The chemical kinetics of $TiCl_4$ oxidation have been represented in the literature by two chemical mechanisms: one-step and detailed. The one-step mechanism considers only an overall reaction for Ti oxidation:

$$TiCl_4(g)+O_2(g)\longrightarrow TiO_2(s)+2Cl_2(g). \tag{1}$$

The rate for this reaction has been studied experimentally by Pratsinis et al. (1990) in the temperature range between 700 °C and 1000 °C and $TiCl_4$:O_2 concentration ratios from 1:1 to 1:20. The rate expression has a first-order dependence on $TiCl_4$ and zero-order dependence on O_2 up to a 10-fold excess. For higher O_2 concentrations, the rate is half order with respect to O_2. The reactions on the surface have also been modeled assuming that the single-step reaction and the rate for surface reaction are found from experiments done by Ghoshtagore (1970) in the temperature range of 400–850 °C. Generally speaking, the one-step mechanism predicts almost instantaneous conversion to TiO_2 once the precursor approaches the flame temperature.

On the other hand, the detailed mechanism (West et al., 2009) has been developed using density functional theory (DFT) based quantum calculations. The detailed mechanism contains 30 species and 66 reactions to describe the Ti oxidation process. The intermediate species undergo reactions such as thermal decomposition, radical abstraction and disproportionation, oxidation and dimerization (West et al., 2007a). Hence, this mechanism