MULTISCALE MODELING OF TiO_2 NANOPARTICLE PRODUCTION IN FLAME REACTORS: EFFECT OF CHEMICAL MECHANISM

Maulik Mehta[a], Yonduck Sung[b], Venkat Raman[b], Rodney Fox[a]
[a]Iowa State University
[b]The University of Texas at Austin

Summary

For titanium dioxide nanoparticles manufactured in flame reactors, the precursor is injected into a pre-existing flame exposing it to a high-temperature gas phase, leading to nucleation and particle growth. Predictive modeling of this chemical process requires simultaneous development of detailed chemical mechanisms describing gas-phase combustion and particle evolution as well as advanced computational tools for describing the turbulent flow field and its interactions with the chemical processes. Here, a large-eddy simulation (LES) computational tool for flame-based titanium dioxide synthesis is developed and a flamelet model representing detailed chemistry for particle nucleation is proposed. The effect of different chemical mechanisms (i.e., one-step, detailed, flamelet) on the prediction of nanoparticle nucleation is investigated using a plug-flow reactor (PFR) and a partially stirred tank reactor (PaSR) to model the flow field. The flamelet model is incorporated in the LES tool and compared to predictions using the one-step model. The LES computational tool is employed to study the effect of the precursor injection configuration on nanoparticle formation.

Keywords

Multiphase and particulate reactors, Multiscale analysis, Complex reacting flows, Nanotechnology applications, High value-added products.

Introduction

Nanoparticles have numerous applications in drug delivery, catalysis, energy and semiconductors. Titanium dioxide (TiO_2) nanoparticles are traditionally used as pigments but have found use in diverse areas like photocatalysis and in reducing nitrogen oxide emissions. The production of TiO_2 by combustion of titanium tetrachloride ($TiCl_4$) is an important industrial process. Although widely used in industry, the process is not well understood and process optimization is based mostly on experiments. Thus, gaining fundamental insight into flame reactors will lead to the manufacturing of nanoparticles with more tightly controlled product properties and minimal variability. Previous modeling work has demonstrated that gas-phase reactions, which lead to particle nucleation and surface growth, and particle aggregation and sintering, are all important in determining the final product properties. Most models for TiO_2 production in the literature use a one-step reaction[2], and thus are unable to describe nucleation processes involving intermediate species.

In a flame reactor, the precursor is transported by a turbulent flow field, and encounters a spatially varying gas composition, depending on the precursor injection configuration. Both precursor transport and reaction history determine the product particles. The flow structure and turbulence are of major importance as they determine species transport and reactant mixing, flame quenching, and particle properties such as polydispersity, morphology, homogeneity, and crystallinity. The accurate modeling of flame reactors requires coupling of detailed chemistry with a detailed flow solver.

Large-eddy simulation

Large-eddy simulation (LES) has emerged as a predictive modeling approach for turbulent reactive flows. LES resolves all large-scale features of the flow, while the small-scale processes are modeled. For flame reactors, both nanoparticle evolution and turbulent combustion have to be modeled. In this work, the nanoparticle population is tracked using a moment-based approach[1]. The LES solver uses a fractional time-stepping procedure to evolve the low-Mach number momentum and continuity equations[2]. Scalar transport equations are solved using a third-order upwind scheme.

Chemical mechanism

Spicer et al.[3] used an overall oxidation rate constant with the surface growth expression given by Goshtagore[4] to propose a nucleation expression based on the one-step reaction:

$$TiCl_4 + O_2 \rightarrow TiO_2 + Cl_2$$

This reaction does not take into account the role of intermediate species encountered in flame reactors. Recently, West et al.[5] proposed a thermodynamically consistent mechanism for $TiCl_4$ oxidation containing 30 species and 66 reactions Thermodynamic equilibrium studies based on the mechanism of West et al.[6] suggest that at temperatures above 600 K the critical nucleus size contains at least five Ti atoms. However, this mechanism does not include any species involving more than three Ti atoms, and must be augmented to predict nanoparticle nucleation. For this purpose, three reactions:

$$Ti_2O_2Cl_4 + Ti_3O_4Cl_4 \rightarrow Ti_5O_6Cl_8$$
$$Ti_2O_2Cl_5 + Ti_3O_4Cl_4 \rightarrow Ti_5O_6Cl_8 + Cl$$
$$Ti_2O_2Cl_6 + Ti_3O_4Cl_4 \rightarrow Ti_5O_6Cl_8 + Cl_2$$

are added to the mechanism of West et al.[1] to model nucleation. This mechanism, along with GRI-Mech 2.11 for methane combustion, is referred to as the detailed kinetic mechanism.

Flame reactor model

The detailed kinetic mechanism is intractable for coupling with LES of a turbulent flame, and thus a flamelet approximation can be used. In flamelet approximation the species mass fractions are only a function of the scalar dissipation rate and the boundary conditions and hence can be precomputed and tabulated in terms of these quantities[7]. A mixed representation combining the flamelet approach for the combustion and detailed/reduced chemistry for Ti oxidation can be used. Here, the predictions of nanoparticle number density ($\#/m^3$) with one-step and detailed chemistry in a plug-flow reactor (PFR) model are compared (Fig. 1). Next, in order to have more realistic flow conditions, the accuracy of combining the flamelet approach for the combustion and one-step/detailed chemistry for Ti oxidation is studied in a partially stirred reactor (PaSR). Also a fully flamelet approach for representing chemistry is investigated on a PaSR. Finally, the flamelet model for the detailed chemistry is compared to the one-step model for LES of a turbulent flame reactor. The flow configuration consists of a coaxial injector with methane in the center and air on the outside[8]. The precursor is premixed with the methane stream. Fig. 2 shows the instantaneous distribution of the particle number density. It can be seen that the particles are formed immediately downstream of the injector. It is important to note that the number density varies by more than 15 orders of magnitude in the computational domain. The effect of chemical mechanism will be discussed in the full paper.

Acknowledgement

The authors would like to thank Prof. Pratsinis (ETH Zurich) for many discussions and also for providing the experimental data used for validation. This work is supported through NSF grant CBET- 0730612.

References

(1) Marchisio D.L.; Vigil R.D.; Fox R.O. Implementation of the quadrature method of moments in CFD codes for aggregation-breakage problems. *Chem. Engng. Sci.* **2003**, 58, 3337.

(2) Akselvoll K.; Moin P. Large eddy simulation of turbulent confined coannular jets. *J. Fluid Mech.*, **1996**, 315, 387.

(3) Spicer, P. T.; Chaoul, O.; Tsantilis, S.; Pratsinis, S. E. Titania formation by $TiCl_4$ gas phase oxidation, surface growth and coagulation. *Aerosol Sci.* **2002**, 33, 17.

(4) Goshtagore, R. N. Mechanism of heterogeneous deposition of thin film rutile. *J. Electrochem. Soc.: Solid State Sci.* **1970**, 117, 529.

(5) West R. H.; Shirley A. R., Kraft M; Goldsmith C.F.; Green W.H. A detailed kinetic model for combustion synthesis of titania from $TiCl_4$. *Combust. Flame* **2009**, 156, 1764.

(6) West R. H.; Beran G. J. O.; Green W. H.; Kraft M. First-principles thermochemistry for the production of TiO_2 from $TiCl_4$. *J. Phys. Chem. A* **2007**, 111 (18), 3560.

(7) Pitsch H. Large-eddy simulation of turbulent combustion. *Annu. Rev. Fluid Mech.* **2006**, 38, 453.

(8) Pratsinis S.E.; Zhu W.; Vemury S. The role of gas mixing in flame synthesis of titania powders. *Powder Technol.* **1996**, 86, 87.

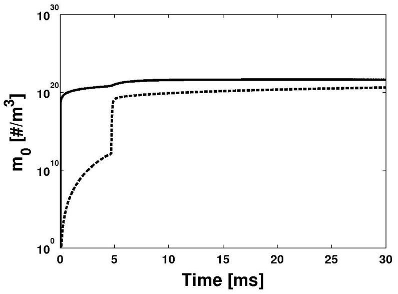

Figure 1. Number density for one-step (solid) and detailed (dashed) mechanisms.

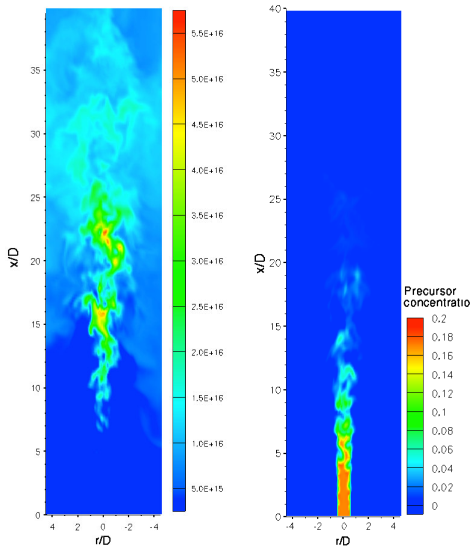

Figure 2. LES results for the (left) nanoparticle number density and (right) precursor concentration.