A MULTICOMPONENT SECTIONAL MODEL APPLIED TO FLAME SYNTHESIS OF NANOPARTICLES

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Sodium/halide flame synthesis and encapsulation (SFE) is a promising technique for producing non-oxide materials. The reaction produces nanoparticles of the core product and a condensable by-product (e.g., NaF). In this research, the SFE process was studied numerically for a spherically symmetric non-premixed flame in a low-pressure atmosphere of sodium vapor. Experimentally, this flame can be established in microgravity. A transient flame code incorporating detailed chemistry and transport processes was developed to perform the investigation. In addition, a two-component sectional method was developed and integrated into the flame code to simulate aerosol dynamics, including coagulation and condensation. For the simulation, the reaction of CF\textsubscript{4} with Na was chosen such that solid carbon was the core product and NaF was the condensable by-product. The results show that near the reaction region, a large number of core particles form, yet condensation of the condensable species does not occur because of the high temperature. Slightly away from the reaction region toward the ambient, there is a narrow region within which rapid condensation of NaF occurs and a few large, heavily coated particles are formed. Most of the small core particles are not coated in this region, but instead are being scavenged by the large, heavily coated particles. Condensation is negligible further downstream because the concentration of the condensable species becomes too low. The simulation also shows that thermophoresis is important, especially at low pressure, to the distribution of particles and that the effect of sticking coefficient on NaF(l) is minimal. The effect of pressure also has been studied, and the results show that the mass fractions of carbon and NaF(l) are insensitive to pressure.

Introduction

Gas-phase combustion synthesis is a promising process for the production of nanoparticles in the growing nanostructure materials industry. Challenges that must be addressed for successful application of this technology include control of particle size, prevention of hard agglomerates, and, if non-oxides are synthesized, protection of the particles from oxidation and/or hydrolysis during postprocessing. Sodium/halide flame synthesis and encapsulation (SFE) is a unique technology that can address these challenges [1–3]. This process incorporates the reaction between sodium and a metal halide in a diffusion flame, resulting in nanoparticles that are encapsulated in salt. Salt encapsulation has been shown to be effective in the control of particle size and morphology. In addition, the salt serves as a protective coating medium that preserves the purity of the core particles during postflame handling and processing. Materials that have been produced using this technology include Al, W, Ta, Ti, TiB\textsubscript{2}, AlN, and composites of W-Ti and Al-AlN [1–3].

The oxygen content of SFE-synthesized AlN nanoparticles encapsulated in salt has been measured by neutron activation analysis and found to be as low as 0.54 wt.% [1], as compared to over 5 wt.% for unprotected AlN of comparable size [4].

To understand the SFE technique, a Monte Carlo simulation has been carried out to simulate the aerosol dynamics of the encapsulation process in a homogeneous system with fixed rate of heat loss [5]. It was found that in a system subject to a modest heat loss of 1–5 W/cm\textsuperscript{2}, the SFE process consists of three steps. First, the particles that form at the flame evolve through coagulation and coalescence. Then, as the temperature drops, the salt vapor condenses onto the larger particles such that these particles quickly become very large. Finally, these coated particles scavenge the uncoated small particles. Although the results of this simulation provide valuable insight into the SFE process, the assumption of homogeneity limits its applicability. Transport processes including convection, diffusion, and thermophoresis are important to the SFE process.
To study the effects of transport, a spherical diffusion flame geometry is employed [6.7]. In normal gravity, buoyancy distorts the flame, and it is not possible to obtain spherical symmetry. In microgravity, a spherically symmetric sodium/halide diffusion flame can be established by ejecting the halide vapor from the burner into a quiescent atmosphere of sodium vapor and argon. In this configuration, transport occurs only in the radial direction. This simple geometry allows simulation of the flame behavior through a detailed description of chemistry, transport, and particle dynamics with limited computational resources. Comparisons between experimental and numerical results are also possible.

Multicomponent aerosol dynamics is key to understanding the SFE process, and in this work, a multicomponent sectional method is developed to study the sodium/halide flame and encapsulation process in a spherically symmetric diffusion flame. In the next section, the flame configuration and the model development will be described. This will be followed by a discussion of results and concluding remarks.

Formulation

The problem to be studied is a non-premixed sodium/halide flame stabilized by a spherical porous burner. A vaporous mixture of halide and argon is issued from the burner into a combustion chamber filled with a mixture of sodium vapor and argon.

The halide chosen for this study is carbon tetrafluoride (CF$_4$), with the overall reaction given by

$$4 \text{Na}(g) + \text{CF}_4(g) \rightarrow \text{C}(s) + 4 \text{NaF} \hspace{1cm} (1)$$

Carbon tetrafluoride is attractive from an experimental perspective because it exists as a gas at standard conditions, is stable at elevated temperatures, and is less hazardous than most halides. Moreover, the basic characteristics of the encapsulation process are not sensitive to the choice of halide. Thus, understanding gained from synthesis and encapsulation of carbon can be applied to other materials. An additional advantage for the use of CF$_4$ is that nanocarbon particles are not reactive in air, so that they can be extracted from the flame and examined by electron microscopy to determine their morphology.

A transient problem was chosen for the simulation to allow for comparison with future experimental data to be obtained in the NASA 2.2 s drop tower. The corresponding equations governing the conservation of energy and gas species are

$$\rho c_p \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \lambda \frac{\partial T}{\partial r} \right) - \rho u c_p \frac{\partial T}{\partial r} - \sum_{k=1}^{K_g} \frac{c_{fp} Y_k V_k}{M_k} \frac{\partial T}{\partial r} + S_c \hspace{1cm} (2)$$

$$\rho \frac{\partial Y_k}{\partial t} = - \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \rho Y_k V_k \right) - \rho u \frac{\partial Y_k}{\partial r} + M_k \dot{\omega}_k + S_{g,k}, \hspace{1cm} k = 1, 2, \ldots, K_g \hspace{1cm} (3)$$

where $T$ is the temperature, $Y_k$ and $M_k$ the mass fraction and molecular weight of species $k$, $r$ the time, $r$ the radial spatial coordinate, $u$ the radial velocity, $\rho$ the gas density, $c_p$ the specific heat at constant pressure, $\lambda$ the heat conductivity, $h_k$ and $\dot{\omega}_k$ the specific enthalpy and production rate of species $k$, $V_k$ the diffusion velocity of species $k$, and $K_g$ the number of gas-phase species. In addition, $S_{g,k}$ is the condensation rate of the condensable species and $S_c$ is the heat of condensation given by

$$S_{g,k} = \sum_{l=1}^{N} \left( \frac{dQ_{lk}}{dt} \right)_{\text{cond}},$$

$$S_c = - \sum_{k=1}^{K_g} h_{lk} \sum_{l=1}^{N} \left( \frac{dQ_{lk}}{dt} \right)_{\text{cond}} \hspace{1cm} (4)$$

where $h_{lk}$ is the latent heat of species $k$, $Q_{lk}$ is the mass of component $k$ in section $\ell$, and $N$ is the number of sections. The inclusion of $S_{g,k}$ and $S_c$ provides the coupling between the gas-phase processes and particle dynamics. Radiation is not considered in this study.

The equations will be solved subject to the following boundary conditions

$$r = r_b, \hspace{1cm} T = T_b, \hspace{1cm} Y_k = Y_{kb} \hspace{1cm} k = 1, 2, \ldots, K_g$$

$$r = r_w, \hspace{1cm} T = T_w, \hspace{1cm} Y_k = Y_{kw} \hspace{1cm} k = 1, 2, \ldots, K_g \hspace{1cm} (5)$$

where the subscripts $b$ and $w$ refer to the given conditions at the burner surface and chamber wall, respectively. Because the chamber is much larger than the flame, the conditions at the chamber wall can be assumed to remain unchanged during the 2.2 s of drop tower time.

Gas-Phase Chemistry

With no reaction mechanism available in the literature for equation 1, a mechanism that involves a simple sequential abstraction of fluorine by sodium is proposed, as shown in Table 1. The reasoning follows that of Ref. [8]. Realizing that the abstraction reactions of CF$_4$ in Na are similar to those of TiCl$_4$, their pre-exponential factors are expected to be similar, so that the values for TiCl$_4$/Na reactions [8] are adopted. It is also assumed that for endothermic reactions, the activation energies are equal to the enthalpicities of the reactions as provided by the JANAF tables [9]. The sodium/halide system is diffusion-limited, so uncertainty in the kinetic mechanism is not expected to significantly affect the goal of this work, which is to study encapsulation. Indeed, no significant change in results was observed when the pre-exponential factors were decreased by two orders of magnitude.
Aerosol Dynamics

The aerosol process involves particle generation by nucleation and particle growth through coagulation and condensation and will be studied by the sectional method. The procedure is to divide the aerosol size spectrum into sections and assume that in each section the mass distribution of the particles has a prescribed function, in this case, a uniform distribution. For multicomponent aerosols, it is further assumed that all particles in a section have identical composition. For a system with $s$ components and $N$ sections, there are $s \times N$ variables to be solved.

In the sectional method, we solve for the total mass of each component in every section. The composition of particles in a given section is then determined by the mass of each component in that section. Condensation will move mass of both components into larger sections. In other words, the position of particles in a given section is then determined by nucleation and particle growth through coagulation and condensation and will be studied by the sectional method. The procedure is to divide the aerosol size spectrum into sections and assume that in each section the mass distribution of the particles has a prescribed function, in this case, a uniform distribution. For multicomponent aerosols, it is further assumed that all particles in a section have identical composition. For a system with $s$ components and $N$ sections, there are $s \times N$ variables to be solved.

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The equation governing the balance of mass concentration of component $k$ in section $l$, $Q_{lk}$, is given by [10]

$$
\frac{dQ_{lk}}{dt} = \frac{1}{2} \sum_{i=1}^{l-1} \sum_{j=1}^{l-1-i} \left[ \beta_{ij} Q_{ij} Q_l + \beta_{ji} Q_{ji} Q_l \right] - \frac{1}{2} \sum_{i=1}^{l-1} \left[ \beta_{il} Q_{il} Q_l + \beta_{li} Q_{li} Q_l \right] - \frac{1}{2} \beta_{il} Q_{il} Q_l - Q_l \sum_{i=1}^{l-1} \beta_{li} Q_i + \alpha G_{il} Q_l - \sum_{i=1}^{l-1} \left[ G_{il} Q_i - \alpha G_{i-1,l} Q_{i-1,l} \right] + \alpha G_{ll} Q_{l-1,l} + S_l
$$

where the $\beta$s are the sectional coagulation coefficients, $Q_l$ the total mass in the $l$th section, $\alpha G$s the intrasectional condensation growth coefficients, $G$s the sectional coagulation coefficients, and $S$s the production rate of the particles. The expressions for $\beta$s are given in [10], and the $G$s are given in [5]. These expressions conserve both mass and number during condensation [11]. The first four terms on the right-hand side account for the change of mass due to coagulation, the next three terms give the change of mass due to condensation, and the last term is the mass production rate of particles through chemical reaction. Carbon particles produced from the reaction given in equation 1 are assumed to be initially 0.2 nm in diameter.

Conservation Equations for Particles

Conservation for particles is described by the mass fraction of condensed species $k$ in section $l$, $Y_{lk} = Q_{lk}/\rho$ given by

$$
\rho \frac{dY_{lk}}{dt} = -\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \rho Y_{lk} (V_{Tl} + V_{Tl}) \right] + \frac{\rho u}{r} \frac{dY_{lk}}{dr} + \frac{dQ_{lk}}{dt}
$$

$$
k = 1, 2, \ldots, s, \quad l = 1, 2, \ldots, N \quad (8)
$$

which is solved subject to the same boundary conditions as those in equations 5–6 for $Y_k$. In equation 8, $V_{Tl} = -D_l \ln(\rho T_l)/\rho$ is the diffusion velocity of the particles in section $l$, where $D_l = k_B T C_l/(3 \pi d_p)$ is the diffusion coefficient of the particles, $\mu$ the viscosity of the gas, $k_B$ the Boltzmann constant, $d_p$ the diameter of the particle, and $C_l$ the Cunningham slip correction [12] given by $C_l = 1 + K_l[1.246 + 0.42 \exp(-0.87/K_l)]$, where $K_l = 2 \lambda_p/d_p$ is the Knudsen number and $\lambda_p$ the mean free path of the gas.

The effect of thermophoresis is included in equation 8 through the thermophoretic velocity in section $l$, $V_{Tl} = F_l B$, where $F_l = -P_l \rho d_p^2 (\partial ln T/\partial r)$ is the thermophoretic force for particles in the transition and free-molecule regimes [13]. Here, $P$ is the gas pressure and $B$ is the particle mobility defined as $B = SC_l/[\pi C_l \rho d_p^2 (v_p - u)]$, where $C_l = 24/Re_p$ is the drag coefficient on a particle in the Stokes regime ($Re_p < 0.1$), $v_p$ the particle velocity, and $Re_p = \rho d_p^2 |v_p - u|/\mu$ the particle Reynolds number.

Description of the Code

Discretization of the differential equations is performed by conventional finite differencing techniques with non-uniform mesh spacing. In each of the equations, the transient term is replaced by an explicit forward difference formula, the diffusive terms by a central difference formula and for better convergence, the convective terms by an upwind difference formula. The discretized equations are solved by Sandia’s Twopnt [14], a code using Newton’s method to solve discretized transient and steady-state boundary value problems. The Sandia
Chemkin and Transport packages [15,16] are incorporated to evaluate chemical reaction rates as well as thermodynamic and transport properties. Non-uniform grids are used in the simulation, and the number of grids is increased until the solution does not change with the addition of grids. The time step also is adjusted until a convergent solution is obtained.

Results and Discussion

For this simulation, results are presented where the chamber pressure is 130 mm Hg (0.17 atm), the mass flow rate is 32.9 mg/min, the CF$_4$ molar fraction at the burner surface is 0.15, the molar fraction of Na at the wall is 0.16, the radius of the burner is 0.318 cm, the radius of the chamber is 10 cm, and the temperatures on the burner exit and the chamber wall are both 893 K. These conditions were chosen to be consistent with the experiments being performed at the NASA GRC 2.2 s drop tower. To first obtain a conceptual view of the flame, Fig. 1 shows results at 1 s assuming all species are gas phase. As seen in Fig. 1, the reactants are consumed at the flame, while carbon and NaF vapor are produced. The maximum temperature is about 1503 K and, consistent with experiment, the flame is about 0.78 cm from the burner exit.

Computations were performed to determine the number of sections required to yield accurate results. The mass concentration of carbon and liquid NaF, as well as the number density of particles at 2 s, were examined. The results show that with just one section per decade, the spatial distribution of aerosol mass has converged, indicating that the sectional method is highly effective at describing mass distribution for this system. At least six sections per decade are needed, however, to ensure accuracy of number density calculations and to resolve the mass distribution of particles at a given spatial location.

To understand the process of NaF condensation, the distributions of temperature and NaF vapor are plotted in Fig. 2 for $t = 1$ s. Also shown in this figure are two regions in which condensation occurs: a primary condensation zone (region I) and a secondary condensation zone (region II). At the left boundary of region I, the NaF vapor becomes supersaturated as a result of the decrease in temperature and condenses onto the carbon particles formed in the reaction zone. At the right edge of this region, condensation of NaF vapor is insignificant because the NaF vapor has been depleted and the NaF partial pressure is low. A similar behavior is observed across region II. Because of the heat released from condensation, the flame temperature is about 200 K higher than that of Fig. 1, where condensation was not included.

Results are presented by first showing in Fig. 3 the evolution of the aerosol during the first 2 s. Mass concentration distributions of C(s) and NaF(l) as well as the temperature profile are plotted at three different times. Thermophoresis is not included in this calculation so that the effect of thermophoresis can be subsequently understood. Furthermore, for clarity, condensation in region II is not included in the model for this plot. Near the flame where the temperature is high (about 0.8 cm from the burner exit), all NaF is in the vapor phase and no carbon particles are coated. At larger radial positions, the temperature decreases, condensation of NaF occurs, and the particles are heavily coated, as exhibited by the high concentration of NaF(l) and low concentration of C(s). The broadening of both concentration profiles, the increase in the maximum amount of NaF(l), and the increase in temperature with time
are attributed to the continuous condensation of NaF. This figure also shows that at the end of 2 s, the system is far from steady state. The particles are still evolving through coagulation and condensation and being carried outward.

Because of the high temperature gradients and low pressure in this system, the flame response is strongly affected by thermophoresis. Results show that the thermophoretic velocities can be as high as several centimeters per second, much greater than the diffusive and convective velocities in most regions. To illustrate its importance, a solution that includes thermophoresis is shown in Fig. 4 by plotting the distribution of $C(s)$ and NaF(l) mass concentrations at $t = 1$ s. Condensation in both region I and II is included in the model for this and subsequent figures. Comparing Figs. 3 and 4, it is observed that with the presence of the thermophoretic force, the particles are driven away from the flame toward both the porous sphere and the chamber wall. This results in a reduction in the maximum concentrations for $C(s)$ and NaF(l) and expanded regions in which these components are found. The effect of thermophoresis on the mass concentration of NaF(l) in region I is primarily to transport the mass outward, as indicated by its being located farther from the burner. Also evident from this figure is that thermophoresis can cause there to be considerable mass at the burner surface, that is, particle deposition on the porous sphere. Nonetheless, the buildup is not sufficient to clog the burner or modify the flow field by the end of the drops.

In Fig. 5, the mass distribution of particles is shown for two different radial positions at $t = 1$ s. The number density of particles is also plotted in Fig. 5b. At 1.1 cm away from the burner exit (Fig. 5a), the particles are uncoated, as there is no NaF(l) in this region and the mean size is around 50 nm. At 2.3 cm (Fig. 5b), some particles are heavily coated with NaF, having a mean size around 300 nm, as evidenced by a high mass concentration of NaF(l). Some small particles are uncoated, and although the mass of the uncoated particles is small, the number density is high because of their small size. As shown in Fig. 2, at $t = 1$ s, condensation region I is between 1.9 and 2.2 cm, indicating that practically all the NaF has condensed at 2.3 cm. The evolution of the aerosol, which involves a small number of large heavily coated particles and a large number of small uncoated particles, is a scavenging process.

The sticking coefficient ($\alpha$) for NaF is not known and can be any value between 0 and 1. In the previous discussions, a value of $\alpha = 0.1$ was adopted. To study the effect of $\alpha$, additional computations using $\alpha = 0.001$ were made, and the results are presented in Fig. 6. This figure shows that the effect of $\alpha$ on NaF(l) is only minimal, which indicates that condensation of NaF occurs relatively fast when the temperature decreases and the amount of NaF(l) is determined by the diffusion rate of NaF vapor into the condensation region. The higher $C(s)$ concentration with smaller $\alpha$ between 2 and 3 cm is due to a transient effect in the first several milliseconds that is transported downstream. For the larger $\alpha$, the condensation rate is higher and the temperature increases quickly due to condensation heat release. The temperature gradient quickly becomes large enough that thermophoresis becomes important and drives particles away from the flame. On the other hand, with a smaller $\alpha$ the temperature increases slowly, and since the reaction rate is not a strong function of temperature, the concentration of $C(s)$
Fig. 5. Mass distribution of particles at (a) 1.1 cm and (b) 2.3 cm away from burner at $t = 1$ s. Number density is also shown in (b).

Fig. 6. The effect of sticking coefficient. Results are at $t = 1$ s with a sticking coefficient of 0.1 and 0.001.

The aerosol dynamics may be sensitive to variations in chamber pressure. To assess the effect of pressure, computations also were made using a pressure of 0.27 atm. The mass fractions of C(s) and NaF(l) do not change significantly with pressure. The primary difference is that the C(s) and NaF(l) profiles are closer to the burner at higher pressure because the thermophoretic velocity decreases with pressure. The temperature distributions are similar for the two pressures because the initial mass fractions of the reactants remain unchanged. There is a slightly higher peak temperature at higher pressure because condensation occurs in the region closer to the flame and the heat released from condensation increases the flame temperature. On the other hand, at lower pressure, the condensation zone is further away from the flame, and this results in a higher temperature in this region.

**Concluding Remarks**

In this study, a flame code with full chemistry and transport was developed to simulate the sodium/balide flame synthesis process in a spherically symmetric CF$_4$/Na flame. A two-component sectional method was also developed and integrated into the flame code to simulate the particle condensation and encapsulation processes. This is the first known work that incorporates multicomponent aerosol modeling with a flame code. The results for the first 2 s of combustion show that near the flame, the temperature is high, such that the salt produced is vapor phase. Downstream of the flame (away from the burner), there is a narrow region in which salt condenses onto carbon particles and a few large, heavily coated particles are formed. A large number of small particles are left uncoated in this region. Further downstream, the particles evolve through a scavenging process in which small particles are scavenged by large, heavily coated particles. The investigation also shows that thermophoresis is important for this process, especially at low pressures. After 1 s, the mean size of the uncoated small particles in the flame zone is predicted to be about 50 nm in diameter, while the large coated particles are about 300 nm in diameter. The study shows that the effect of sticking coefficient on NaF(l) is minimal, which indicates that condensation of NaF occurs relatively fast and the amount of NaF(l) is determined by the diffusion rate of NaF vapor into the condensation region. The study also shows that at lower pressure, the particles are transported further away from the flame because of the higher thermophoretic velocity at low pressure.
Acknowledgments

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REFERENCES


COMMENTS

Markus Kraft, University of Cambridge, UK. How many sections did you use in your sectional methods, and was this number kept constant along the flame? How did the number of sections scale with the computational time?

Author’s Reply. Six sections per decade were used in the sectional method throughout the computational domain. The variables solved in this model include temperature, velocity, gas species concentrations, and mass concentration of particles in each section. Only a portion of the computational time is spent solving the aerosol dynamics equations, and that portion depends on the amount of gas-phase species considered. For a system with few gas-phase species, the computations for the sectional equations consume a majority of the CPU time, and in this case, the computation time scales with the square of the number of sections.

Jürgen Warnatz, Heidelberg University, Germany. Are there no data existing, for example, from molecular beam experiments on the reaction of halogen compounds with Na, K, etc., which could help you to estimate rate coefficients in your reaction mechanism? Are your results sensitive to the reaction mechanism?

Author’s Reply. Our efforts indicate that reaction rate data are not available for the species considered. There are some very old data by M. Polanyi et al. (Ref. [8] in paper) for sodium reactions with various halides, but they are not directly relevant to this work. Fortunately, the results are not sensitive to the accuracy of the reaction mechanism because the system is diffusion limited. We have examined the effect of the reaction mechanism by decreasing the pre-exponential factors by two orders of magnitude and found very little difference in the results.