Chapter 4

Silica aggregate growth in 1-D methane/air flames

Silica aggregate formation was studied in 1-D premixed methane/L2/air flames by angle-dependent light scattering measurements for various siloxane concentrations, flame temperatures and equivalence ratios, using Guinier analysis to interpret the experimental data. Measurements were performed in lean ($\phi = 0.8$), stoichiometric ($\phi = 1.0$) and rich ($\phi = 1.3$) methane/air flames at temperatures ranging from 1800 K to 2100 K and containing 300 to 1600 ppm Si. A sublinear dependence of the aggregate radii of gyration $R_g$ of generated silica particles on residence time, and non-monotonic dependence on flame temperature with maximum around 2000 K have been observed, with radii of gyration $R_g$ in the range of 10 to 120 nm. Furthermore, a lean flame environment appears to foster aggregate growth compared to rich and stoichiometric flames, in which growth is very similar. When fixing the initial conditions at the residence time corresponding to the first measurement point, a simple model describing particle evolution as a result of collisional growth and sintering predicts the functional dependence of the growth of particle radii well.

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4.1. Introduction

As explained in Section 1.3.2, an issue complicating the implementation of biogas in the energy infrastructure is the presence of trace compounds like siloxanes. The deleterious effects on the performance of combustion equipment, caused by the deposition of the silica particles generated by the combustion of siloxane-containing fuels, put limits on acceptable concentrations of siloxane impurities. Because, as discussed above, the structure of these silica aggregates is a major determinant for the impact of deposition in combustion equipment, it is important to understand what happens on the aggregate level.

An analytic approach for describing particle growth [1] can be very instructive, as it provides insight into functional dependencies, but is of limited quantitative value because of the system’s complexity. Similarly, numerical models [2–7] are as yet unreliable because the kinetics of silica aggregate formation is not well known. Therefore, experimental studies to characterize the aggregates are indispensable to gain a better understanding of processes of silica formation in combustion environments.

Previous studies of silica formation in flames have been motivated by synthesis of ceramic powders [8]. In these studies, particle generation has been investigated mainly in diffusion flames at atmospheric pressure [9–16]. Because of the spatially varying temperature and local fuel/oxidizer ratios in these systems, the results of these studies are difficult to interpret unambiguously, particularly regarding processes that occur at relatively short time scales. Furthermore, many of these studies used silane (SiH₄) as the source of silicon. As discussed in Section 2.6, complete premixing of this compound with the fuel-air mixture is problematical due to its pyrophoric nature, and its diffusive introduction gives rise to uncertainties in the actual local concentrations of silica precursors. However, the use of (relatively air-stable) siloxanes has opened the door to premixed studies with well-defined local concentrations. One-dimensional (1-D) premixed flames yield conditions more amenable to analysis and which can be varied in a straightforward manner (see Section 2.2). Using ex-situ particle sampling Smirnov et al. [17], for example, analyzed aggregate growth and primary particle size as function of residence time in this type of flame based on transmission electron microscopy (TEM). Other studies in premixed 1-D flames employed in-situ techniques such as dynamic light scattering [18,19] and angle dependent light scattering (ADLS) [20,21] to characterize silica growth as function of time. In-situ measurements have a clear advantage over ex-situ methods such as TEM in that they obviate the need for intrusive physical sampling. In addition to being more time efficient, in-situ measurement removes the uncertainties related to disturbing the particle growth processes in the flame as a result of sampling.
Previous in-situ studies in 1-D premixed flames also varied a limited number of experimental parameters. For example, Ulrich and Riehl [20] examined different silica concentrations in the fuel/oxidizer mixture and altered the temperatures in a turbulent jet flame by varying the equivalence ratio. They also performed experiments on flames stabilized on a honeycomb flame holder, but the reduction in flame temperature was not characterized. Chang et al. [21] investigated the effect of adding POCl₃ vapor, to depress the melting point of silica, on silica agglomerate morphology. To our knowledge, no studies have been done that systematically vary flame temperature independently from the equivalence ratio, which is readily obtained in 1-D premixed flames [22]. Furthermore, given the interest of the prior studies in the synthesis of ceramic powders, the range of concentrations in studies that examined the effects of precursor concentration [23] are generally above 0.15 mol%. In this chapter, we present results obtained using angle dependent light scattering (ADLS) to study silica aggregate growth in 1-D premixed flames using L₂ as silica precursor (as described in Section 2.6). Here we investigate aggregate growth as a function of residence time for a wide range of experimental conditions, varying silica concentration, flame temperature and equivalence ratio. We emphasize here that the flame conditions considered in this study are those that actually occur in combustion equipment; in fact, the burner configuration used, the residence times covered and the variations examined [24] are nearly identical to those in millions of appliances used for domestic heating. As such, this study contributes towards identifying the conditions germane for silica deposition when burning siloxane-containing biogases.

4.2. Experimental

Silica aggregates were produced in flat, premixed methane/L₂/air flames at atmospheric pressure using the system shown schematically in Figure 2.6. The flames were stabilized above the 60-mm diameter perforated ceramic burner deck of the home-made burner with downstream chimney that was described in Section 2.4.2. Measurements of $R_g$ in the post-flame zone were performed by laser light scattering as detailed in Section 3.2, using the Coherent Sapphire 100 mW laser. The axial distance between the measuring volume and the burner surface (HAB) was varied by moving the burner axially in 5 mm steps.

Flames of various temperatures and fuel equivalence ratios were obtained by setting appropriate air and methane mass fluxes using the gas handling system detailed in Section 2.5. The flame temperature was varied by changing the mass flux through the burner while keeping the fuel/air ratio constant as described in Section 2.2. Three
equivalence ratios, $\phi$, were studied here, $\phi = 0.8, 1.0$ and $1.3$. Since prior studies [22,24,25] showed that the measured maximum temperatures and those determined by solving the one-dimensional governing equations for burner-stabilized flames agree to within 50 K, here we computed the flame temperature. The results obtained by using the code from the Cantera suite [26] with the GRI-Mech 3.0 chemical mechanism [27] are shown in Figure 2.3. In this figure, the mass flux is recast as a linear exit velocity of the 1-D fuel-air mixture, anticipating the conversion to residence times below. Experiments under similar conditions [28] indicate that for the region of measurement examined here (see below) the temperatures were generally constant up to $\sim 30$ mm, followed by a slow decrease. At the lowest mass fluxes described below, axial distance of constant temperature is less than 20 mm. Since the siloxane fractions studied are relatively low, we neglect any contribution of the presence of siloxanes on the computed temperatures.

### 4.3. Dependence of aggregate size on Si concentration

As described in Section 3.2, $R_g$ was obtained from the measured ADLS data. The measured $R_g$ in stoichiometric flames at $T = 1950$ K (see Figure 2.3) are shown in Figure 4.1 as a function of distance above the burner for 300-1600 ppm Si in the combustion products. Stray light limited the measurement to $>10$ mm above the burner surface.

![Figure 4.1](image)

*Figure 4.1. Radius of gyration $R_g$ for 1950 K stoichiometric flames as a function of axial distance above the burner, for 300-1600 ppm Si. Points above the dashed lines rely (partly) on data where $qR_g > \sqrt{3}$.*

Part of the data was acquired outside the regime of $qR_g \leq \sqrt{3}$ for which the fitting procedure is known to yield accurate $R_g$ [28,29]. However, since plots of $I(0)/I(q)$ vs. $q^2$
were found to be linear for these data, we expect the fits to still give reliable values for $R_g$ [29].

As we can see in Figure 4.1, for all siloxane concentrations there is growth of aggregates with increasing HAB. At the highest Si concentration of 1600 ppm, $R_g$ increases from $\sim$40 nm at 10 mm to $\sim$120 nm at 50 mm. The smallest measured $R_g$ is $\sim$15 nm at 25 mm above the burner for 400 ppm Si. For this aggregate size, the signal difference between scattered intensities at the smallest and largest detection angle is less than 2%. Despite the fact that particles at smaller axial distances, where $R_g$ and correspondingly the angular dependence of the scattered signal is even smaller, still generated a scattering signal a few times more intense than that in air, the fitting procedure at these heights typically yielded unreliable results. With increasing Si concentration, the minimum height where the fitting procedure could be used to yield $R_g$ moves closer to the burner surface. We observe that extractive measurements followed by TEM analysis [17] for a stoichiometric flame with $\sim$500 ppm Si at a temperature somewhat higher than here ($T = 2090$ K) gives similar results to those at 500 ppm Si in Fig. 5, particularly when considering the effect of temperature on $R_g$ described below. This consistency gives additional confidence in the scattering results.

Note that the smallest aggregates measured contain very few monomers. Assuming a $D_f$ of $\sim$1.8 [29], an aggregate with $R_g$ of 15 nm would contain only 3 to 18 monomers with radius of 8 or 3 nm respectively. On the other hand, an aggregate with $R_g$ of 120 nm would contain 130 monomers of 8 nm radius.

For further analysis, we estimate the characteristic times of silica particle formation using the simple theoretical considerations laid out in Section 1.2. Decomposition of siloxane proceeds in the flame front, resulting in the formation of SiO$_2$ molecules that condense into small clusters, which in turn collide with other molecules and clusters, as represented by Eq. (1.1). When the corresponding rate $R_{i,j}$ is known, it can be used to find the characteristic time of association of a particle of size $i$ with any particle of size $j$ as $\tau_{i,j} \sim N_i/R_{i,j}$. Assuming a sticking coefficient of unity, the rate of association of two particles is given by $R_{i,j} = \beta_{i,j}N_iN_j$. For the current experimental conditions (1950 K and 1 atm) the free path length $\lambda$, calculated based on air viscosity according to [30], is approximately 550 nm. Thus $\lambda$ exceeds the measured gyration radii (Figure 4.1) by at least 5 times. Because the particle’s radius of gyration is to a good approximation equal to its collision radius, it is therefore reasonable to use the free molecular approximation for estimation of characteristic collision times. If we assume that the particles are monodisperse, we can get a simple estimate of the time of association between two particles. In this case the collision kernel is given by Eq. (1.6), while the number density of particles is
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given by Eq. (1.9). Hence, for a silica concentration of 800 ppm in a 1950 K flame, the characteristic time of association of spherical particles with a 5 nm radius (thus containing \( \sim 16000 \) molecules) is \( \sim 3 \) ms, corresponding to a height of less than 3 mm, implying that the first stage of silica formation is relatively fast and cannot be studied in the present experiment as it is well below our first measurement point at 10 mm (\( \sim 12 \) ms). Results with TEM in a similar flame [17] confirmed formation of fractal structures starts very close to (within 3 mm) the burner surface.

Proceeding further with the analysis along the lines of Section 1.2.2, assuming that all silica is bound in particles, the particle density of combustion products is constant, and that the monomer radius \( a = 3v/s \) is constant in time, we find the time dependence for the collision radius given by Eq. (1.12). Comparison with the data in Figure 4.1 shows that the time dependence for the particle radius thus obtained is in poor agreement with the experimental results. For low silica concentrations, the experimental time dependence of the particle size appears to be approximately linear, and for higher concentrations the curves clearly show a sublinear dependence, in disagreement with Eq. (1.12), which gives a \( t^{1.43} \) dependence for \( D_f \sim 1.8 \). The agreement can be improved by taking \( D_f \) larger than 2, but this is at variance with available experimental observations (see, for example, [19,29,31]). It is clear that this model needs to be refined.

To improve the description of particle evolution we should reconsider our assumption that the monomer size is unchanging throughout aggregate growth. This approximation essentially separates particle growth into two separate stages: monomer growth initially, and the subsequent aggregation of fixed-size monomers. But this assumption ignores the inter-particle monomer growth due to (partial) sintering as an important aspect of aggregate development. As was mentioned towards the end of Section 1.2.2, it is well known that the growth process is actually a combination of particle collisions and simultaneous intra-aggregate fusion. Driven by the tendency to minimize surface energy, contacting monomers inside aggregates will tend to coalesce together into larger spheres, decreasing the total surface area (Eq. (1.13)). This was for example observed in [17], where the monomer radius was seen to increase from an initial 3 nm to 6 nm at 50 mm above the burner. As noted in Section 1.2.2, the sintering rate is a material specific property that is strongly dependent on the temperature and on the sintering mechanism. A variety of expressions have been proposed for the sintering time of silica [32], but to our knowledge none that are expressly applicable to the short residence times and small particle sizes relevant for the first stages of particle growth in this research. As an estimate we use an
expression for bulk silica, based on a viscous flow mechanism, determined by Xiong et al. [3] using data from Kingery et al. [33], given by

$$\tau_s = 1.3 \times 10^{-12} a \exp \left( \frac{8.3 \times 10^4}{T} \right). \quad (4.1)$$

The sintering time according to Eq. (4.1) at 1950 K for monomers with a radius of 5 nm is just under 20 ms. Since this is of the same order as the characteristic residence time in the present experiment (recall that HAB 10 mm corresponds to 12 ms), sintering should be taken into account in our description of particle growth (most other formulas will give even shorter magnitudes for $\tau_s$ [32]). In fact, based on TEM measurements by Smirnov et al. [17] for similar experimental conditions, we expect the monomer radius to more than double over the course of measured growth. Thus the proper analysis of the evolution of silica particles under the present experimental conditions requires solving the system of equations describing both processes of coagulation, and sintering.

Since it is not feasible to solve the equations analytically, we model the system numerically following the procedure described in [34]. In these simulations, Eq. (1.10) is generalized by adding a term taking into account the change in gas density due to a temperature decrease downstream, and Eq. (1.13) is augmented with a term to account for surface growth resulting from the coagulation process. Then the system of equations becomes

$$\frac{dv}{dt} = \left[ \frac{1}{2} \beta N_p - \frac{1}{\rho_{cp}} \frac{d\rho_{cp}}{dt} \right] v , \quad (4.2)$$

$$\frac{ds}{dt} = \frac{1}{\rho_{cp}} \frac{dv}{dt} + \frac{1}{\tau_s} \left[ s - s_{sph} \right] , \quad (4.3)$$

where $\rho_{cp}$ is the density of the combustion products. Because the averaged molecular mass of the combustion products remains constant, we can replace $\rho_{cp}$ in Eq. (4.2) by $1/T$. In the present experiments we have observed a decrease in temperature, which for simplicity is approximated by $T(t) = T_0 \exp(-y t^2)$, with $y = 38 \, s^2$. At 50 mm above the burner surface, the temperature had decreased from 1950 to 1700 K, resulting in a considerably increased sintering time according to Eq. (4.1). Furthermore, we take into account the transition from the free molecule to continuum regime, using Eq. (1.7) for the collision kernel. In our calculations we set a fractal dimension of 1.8, taking into consideration that the evolution of
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$D_f$ from spherical to fractal-like aggregates as described by Goudeli et al. [35] only has a minimal impact on the results.

Starting the simulations at $t = 0$, setting the initial values of $s$ and $v$ to those of spheres with typical molecular radius ($\sim 0.2$ nm), resulted in poor agreement with the experimental data. We attribute this primarily to the uncertainty in the estimation of the sintering time, while the model is highly sensitive to this parameter during the initial stage of aggregate growth. Using Eq. (4.1) for the sintering time results in gross overestimates of the rate of growth of the collision radius, because it apparently underestimates the rate of sintering for short residence times, here at $t_{res} < 10$ ms. The use of other expressions for the sintering time [32] also did not reproduce data, neither in particle size nor functional dependence on residence time. While fitting parameters in functional dependencies for sintering time such as Eq. (4.1) can bring agreement between the experiment and simulations, the lack of experimental data for the first stage of growth, and assumptions made in establishing the current model, dissuades us from following this procedure in the present discussion. It should be pointed out that chemistry could also be a factor during the initial stage of growth, which was not included in the model.

To see whether the simulations can predict the functional dependence shown in Fig. 5, above, without having to predict the initial stages in particle formation, we start the simulations at the residence time corresponding to the first point measured in each series. The initial values of $s = 4\pi r_c^{D_f} a^{2-D_f}$ and $v = \frac{4}{3} \pi r_c^{D_f} a^{3-D_f}$ are set by using the measured value of $R_g$ as the collision radius $r_c$ and adjusting the monomer radius $a$. Furthermore, a scaling factor $c$ was included in Eq. (4.1) for the sintering time $\tau = c\tau_s$. The best agreement between the experimental and calculated $r_c$ for all silica concentrations is achieved with the scaling factor $c \geq 10$, essentially disabling particle coalescence though sintering at times after initial particle formation. The analysis in [15] resulted in a similar conclusion. The results of simulations for 400, 800 and 1600 ppm of silica with the values for $a$ obtained by fitting of 5.5, 4.3, and 3 nm, respectively, are shown in Figure 4.2, where residence times for experimental data were calculated using the measured flow rates and estimated flame temperatures. We see that the experimental data for higher silica concentrations require a smaller value of $a$, while it is expected that the additional available silica would result in larger monomers. At the same time, we point out that even without sintering the model accounts perfectly well for the sublinear time dependence of $r_c$; this is the result of using Fuchs’ interpolation expression for the collision kernel, rather than the free molecular assumption that was used to get Eq. (1.12). We report that the simulated results were relatively insensitive to the temperature history used, as a result of the temperature

4.4. Temperature dependence

The measured gyration radii $R_g$ in stoichiometric flames at temperatures ranging from 1800 K to 2100 K, for a fixed concentration of 800 ppm silica in the combustion products, are shown in Figure 4.3 as a function of residence time. These experimental data show a non-monotonic dependence of aggregate growth on the flame temperature. When the flame temperature increases from 1800 K to 2000 K, $R_g$ increases, reaching a maximum at 2000 K and then decreases again as the flame temperature is increased further. The analysis in [15] resulted in a similar conclusion. The results of simulations for 400, 800, and 1600 ppm of silica with the values for $a$ obtained by fitting of 5.5, 4.3, and 3 nm, respectively, are shown in Figure 4.2, where residence times for experimental data were calculated using the measured flow rates and estimated flame temperatures. We see that the experimental data for higher silica concentrations require a smaller value of $a$, while it is expected that the additional available silica would result in larger monomers. At the same time, we point out that even without sintering the model accounts perfectly well for the sublinear time dependence of $r_c$; this is the result of using Fuchs’ interpolation expression for the collision kernel, rather than the free molecular assumption that was used to get Eq. (1.12). We report that the simulated results were relatively insensitive to the temperature history used, as a result of the temperature
dependence of Eq. (4.1), and were more sensitive to the initial particle size. This emphasizes the need for more experimental information on the initial stages of particle growth.

![Figure 4.2](image)

**Figure 4.2.** Numerical simulations (lines) for silica concentrations of 400, 800 and 1600 ppm obtained by matching the collision radius with the initial data point of each series, the symbols give the measured radii.

### 4.4. Temperature dependence

The measured gyration radii \( R_g \) in stoichiometric flames at temperatures ranging from 1800 K to 2100 K, for a fixed concentration of 800 ppm silica in the combustion products, are shown in Figure 4.3 as a function of residence time.

![Figure 4.3](image)

**Figure 4.3.** Radius of gyration \( R_g \) for stoichiometric flames as a function of residence time \( t_{res} \) with different temperatures; 800 ppm Si in the gases.

These experimental data show a non-monotonic dependence of aggregate growth on the flame temperature. When the flame temperature increases from 1800 K to 2000 K, \( R_g \)
corresponding to a given residence time increases as well, whereas in the temperature range above 2000 K we observe either constant or a slight decrease in $R_g$ at the same residence time with increasing temperature. The smaller $R_g$ for the highest temperatures, which are above the melting point of bulk silica [36], are attributed to fast sintering, resulting in relatively compact particles consisting of large monomers. Interestingly, the opposite does not hold true for temperatures below 2000 K, where in the framework of the model, we would expect the low sintering rates to result in relatively fast formation of large, low-density structures, while the impact of the change in temperature on the collision kinetics is marginal. Given the changes in temperature close to the bulk melting point, the possibility of increased clustering of monomers caused by progressively enhanced viscous attachment as the temperature is raised from 1800 K to 1950 K could stabilize larger clusters more easily than association by van der Waals attraction [35]. However, at the relatively short time scales of the experiment, the sintering rates to coalescence, resulting in denser clusters, are still relatively slow below 2000 K. Another effect, intrinsic to laminar, burner-stabilized flames is possible thermophoretic transport of very small silica clusters upstream from the flame front, even to the burner surface, which can increase when decreasing the mass flux. Although it is unlikely that substantial fractions of the silica particles will be deposited at the burner by this mechanism, additional experiments and detailed modeling will be required to describe this process adequately.

We also note that much practical combustion equipment functions with such variations in temperature at the residence times reported here. Thus, the large variation in particle size when changing operating conditions can impact the rates of silica deposition in practical equipment; this also suggests operating regimes may exist for equipment intended to minimize the effects of deposition, which will be investigated in the future.

Using the numerical simulations described in the previous section, we could achieve fits of comparable agreement as seen in Fig. 6, when varying the monomer radius $r_m$. For temperatures of 1850, 1950 and 2050 K, the “best fit” monomer radii, $\alpha$, are 6.2, 4.3, and 5.8 nm, respectively, which reflect the non-monotonic dependence of $r_c$. The larger $\alpha$ for 2050 K compared to 1950 K corresponds with the expectation of more compact particles, but the suggestion indicated by [37], that changes in nucleation lead to larger particles at relatively low temperatures, seems at present the only explanation for the larger $\alpha$ for 1850 K. Other experiments, in which the monomer radius is measured at low Si concentration and short residence times, are required to better explain the observed influence of temperature on particle growth.
4.5. Dependence of aggregate growth on equivalence ratio

As mentioned in Section Chapter 4, most of the experiments on premixed flames have varied the flame temperature together with the equivalence ratio. Here we maintain the flame temperature by changing the mass flux through the burner as explained in Section 2.2. Aggregate growth was studied in lean ($\phi = 0.8$), stoichiometric and rich ($\phi = 1.3$) flames at 1850 K and 1950 K, doped with 800 ppm Si. The results, presented in Figure 4.4, show a remarkable difference between particle growth in a lean flame environment on the one hand, and stoichiometric and rich environments on the other. The oxygen-rich environment appears to greatly stimulate aggregate growth, up to a factor of 2 as compared to the other equivalence ratios, while there is no significant difference between particle growth in stoichiometric and fuel-rich (oxygen-poor) flames. Comparison with stoichiometric flames of higher temperatures (e.g., as in Figure 4.3) shows that the observed difference is well in excess of what might reasonably be attributed to a slight variation in flame temperature due to the small uncertainty in conditions.

![Figure 4.4. Radius of gyration $R_g$ as function of residence time $t_{res}$ at 1850 K (left) and 1950 K (right) for three equivalence ratios; doping of 800 ppm Si.](image)

Because there is little difference in transport properties between the combustion products at different equivalence ratios, the model described above will not reflect a dependence on equivalence ratio. There are very few published studies that examine particle growth with a comparable variation in parameters. In [38], particle formation was also considered in a very rich premixed ($\phi = 3$) H$_2$/O$_2$ flame doped with L2, where they raised the possibility of other silicon-containing species such as SiO condensing with the particles. Although simple equilibrium calculations indicate that silica should be the major
condensed species, even at $\phi = 1.3$, it is premature to exclude kinetic effects in silica formation for the temperatures and residence times presented here. Conditions of excess oxygen, in which we expect SiO$_2$ to be the only condensing species, appear to foster particle aggregation, particularly at lower temperatures where we expect sintering to be relatively slow, as described above. For conditions of low oxygen, a mechanism by which SiO or other species [38] deposits with silica in the primary particles either inhibits aggregate growth, particularly at lower temperatures, or (strongly) enhances sintering to generate denser particles. Measurement of primary particle size is necessary to discriminate between these mechanisms.

### 4.6. Summary and conclusions

ADLS measurements in 1-D premixed methane/hexamethyldisiloxane/air flames showed a sublinear dependence of the radii of gyration $R_g$ of generated silica particles on residence time, and a non-monotonic dependence on flame temperature with maximum around 2000 K. Interestingly, a lean flame environment appears to foster aggregate growth compared to rich and stoichiometric flames having comparable growth. This result implies an unexpected dependence of aggregate formation on oxygen fraction and warrants further research, both to explore regimes for influencing particle growth [20] and to assess the impact of silica formation and deposition in practical combustion equipment [39,40]. The results presented here recommend caution when altering the equivalence ratio as a means to study the effect of flame temperature on particle growth.

Using a simple model to describe particle evolution from $t = 0$ as a result of collisional growth and sintering was frustrated by the lack of an accurate expression for the sintering time, for the time scales and particle sizes in the experiment, and an incomplete understanding of the first stages of particle growth where chemistry may still be relevant. Using initial conditions derived from the experimental data, at times greater than $\sim$10 ms, the model describes aggregate growth adequately, but suffers from the necessity of fitting the monomer radius. It is crucial to acquire more data for the initial stage of growth to explain the observed dependence of $R_g$ on temperature and equivalence ratio. Future TEM measurements could serve to augment the ADLS-acquired experimental data, particularly to characterize the development of monomer size. This would also allow for determination of $D_f$ and the average number of monomers in fractal aggregates for the flame conditions considered here.
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At $\phi = 1.3$, it is premature to exclude kinetic effects in silica formation for the temperatures and residence times presented here. Conditions of excess oxygen, in which we expect SiO$_2$ to be the only condensing species, appear to foster particle aggregation, particularly at lower temperatures where we expect sintering to be relatively slow, as described above. For conditions of low oxygen, a mechanism by which SiO or other species [38] deposits with silica in the primary particles either inhibits aggregate growth, particularly at lower temperatures, or (strongly) enhances sintering to generate denser particles. Measurement of primary particle size is necessary to discriminate between these mechanisms.

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References


Chapter 5

Effects of hydrogen addition on silica aggregate growth

The effects of hydrogen addition on silica growth in burner-stabilized methane/air flames with low fractions of L2 are reported. Profiles of the aggregates' radius of gyration $R_g$ and monomer radius $a$ versus residence time were measured by laser light scattering. Experiments were performed at equivalence ratios of 0.8, 1.0 and 1.3, with mole fractions of 0 – 0.4 of hydrogen in the fuel. At equal mass flux, the addition of hydrogen was found to result in decreasing $R_g$ and $a$. However, keeping the flame temperature rather than the mass flux constant upon hydrogen addition resulted in the same measured profiles.

This chapter is based on the work presented in: Langenkamp PN, Levinsky HB, Mokhov AV. The effects of hydrogen addition on silica aggregate growth in atmospheric-pressure, 1-D methane/air flames with hexamethyldisiloxane admixture. Int J Hydrogen Energy 2018;43:2997–3003.