Using silicon tetrachloride as a precursor, the silica nanoparticles (NPs) were synthesized in the diffusion flame of air and liquid petrol gas (LPG). Different effects on flame shape and temperature, silicon tetrachloride conversion, major gas-phase compositions, and diameter of silica NPs were obtained via thermodynamic, hydrodynamic, or particle-dynamic approaches. The size of silica NPs decreased with the increasing air-flow rate, increased with the increasing LPG flow rate, and increased obviously with the increasing evaporator temperature. The size of the synthesized silica NPs is about 25–30 nm at an optimal condition.

Keywords: gas-phase combustion, silica, nanoparticle, thermodynamics, particle dynamics, hydrodynamics

INTRODUCTION

Gas-phase combustion synthesis has become an established way to produce particles with desired characteristics on an industrial scale (Pratsinis, 1998). One of the commodities produced by this method is silica nanoparticles (NPs).

The nanosized silica is quite attractive since it is an excellent functional material and can be applied in many areas. Scientists are paying much attention to study the properties of silica NPs, for example, the plug flow of silica NPs during fluidization (Chen et al., 2002), the variation of zeta potential (Xu et al., 2003), the thermo-mechanical properties when blended with polyolefin (Preghenella et al., 2005), the magnetic properties of core-shell silica microspheres (Zhu et al., 2003), the radiation effects and surface deformation of silica NPs (Nishikawa et al., 2002), water
evaporation from porous silica NPs fluidized by air (Davidson et al., 2001), etc. Silica NPs can enhance the performance of many materials such as electric sealing materials, polymer composite materials, biological materials, pharmaceuticals, ceramics, and glasses (Rao et al., 2001; Hilliard et al., 2002; Cordelia, 2006). Nowadays, methods for synthesizing silica NPs are attracting great attention.

Approaches for synthesizing silica NPs can be classified into liquid-phase and gas-phase syntheses. For the former, typical examples are the sol-gel processing (Santos et al., 2007), the solution hydrolysis (Donley et al., 2003), and the supercritical method (Heley et al., 1995). For the latter, typical examples are the gas combustion synthesis (Jang, 2001; Linow et al., 2002), the microwave plasma synthesis (Hong et al., 2004), and the RF plasma synthesis (Hong et al., 2003). Furthermore, the diffusion flame synthesis (DFS) could be easily scaled up from laboratory to commercial manufacturing facility. Therefore, many researchers are focusing their attention on the DFS.

In the traditional DFS for preparing NPs, hydrogen (H2) or CH4 was used as the fuel, oxygen as the oxidant, and dried argon as the gas carrier to feed precursor into the high-temperature flame (Zhu and Pratsinis, 1997; Jang, 2001; Mueller et al., 2004). The reaction mechanism is the competition between oxidation and hydrolysis. Zhu and Pratsinis (1997) investigated the silica formation by SiCl4 oxidation in a diffusion flame of methane, the primary particle size was controlled by changing the reactant mixing configuration and oxygen partial pressure. Mueller et al. (2004) synthesized non-agglomerated spherical silica NPs with the diameter of 44–78 nm using oxidation of hexamethyldisiloxane in methane/oxygen diffusion flames. The effect of oxidant flow rate on NPs size was investigated. Though some methods have been industrialized, it is highly expensive due to the comparatively high price of hydrogen and oxygen. In the present investigation, the liquid petroleum gas (LPG) and air were used instead of high price materials to reduce the cost, and the NPs after post-treatment could be used in high-performance tires, paint and printing ink, etc. Thermodynamic, particle-dynamic, and hydrodynamic computations were conducted to simulate the DFS process. The optimal operating conditions were obtained.

EXPERIMENTAL

During the synthesis of NPs by DFS, the nucleation, nuclei growth, and coagulation in the gas phase takes place one after another. The dimension of the combustor and the operating conditions influence the flame temperature and particle residence time, and finally determine the particle size. The experimental flow diagram is illustrated in Figure 1.

There are two gas routes in the combustion system. For the first one, LPG flows through the drier, then flows through the rotameter, and is finally induced into the combustor. For the second one, the compressed air supplied by the compressor flows through the drier, the rotameter, and the evaporator one after another. The silicon tetrachloride and LPG used in the experiments were all industrial grade. The mole contents of the components in LPG are: C2H6, 8.6%; C3H8, 32.4%; cyclopropane, 3.5%; i-C4H10, 20.1%; n-C4H10, 29.3%; butane, 5.6%; others, 0.5% (Segawa et al., 1996). The configuration of the combustor that introduces LPG and air into the diffusion flame is illustrated in Figure 1. The combustor used in the experiments consists of two concentric glass tubes. The diameters of the inner and outer tubes are 3.5 and 9.0 mm, respectively. The thickness of the glass tube is 1 mm, and the length of the combustor is 150 mm. The newly synthesized silica NPs are prone to deposit onto the inner wall of the tube, causing the obstruction of gas flow. Therefore, the outlet of the inner tube was enlarged to avoid the possible obstruction. A ceramic filter placed above the flame was used to capture the synthesized NPs. The production rate of the apparatus was about several grams per hour. After post-treatment at certain conditions, different grades of silica NPs could be obtained.

A transmission electron microscope (TEM, H-600; Hitachi, Tokyo, Japan) was used to measure the size and shape of synthesized NPs. An X ray diffraction (XRD) analyser (D/Max IIIC; Rigaku, Tokyo, Japan) for powders was used to investigate the crystalline structure of NPs using CuKα radiator. The combined water in NPs was characterized using a Fourier transform-infrared (FT-IR) spectroscope (Nicolet Avatar 360), a differential scanning calorimeter (DSC), and a thermogravimeter (TG).

MODEL DEVELOPMENT

With the development of particle dynamics, hydrodynamics, thermodynamics, and computer hardware, it is possible to predict the optimal conditions for synthesizing NPs. The nucleation, nuclei growth, and coagulation of NPs in gas phase could be simulated by particle-dynamic models (Kruis et al., 1993). Some published articles in literature only focused on the oxidation reaction in DFS. In the present investigation, both the oxidation and the hydrolysis reactions were considered in the particle-dynamic simulation. The combustion flame under the experimental conditions was simulated numerically using a hydrodynamic model. Moreover, the compositions of the reaction system were predicted using a thermodynamic model.
Particle-Dynamic Model

Concentration equation

The formation of NPs can be divided into three parts: chemical reactions, particle aggregation, and sintering. The silica monomer concentration was determined by chemical reactions, and the particle diameter was controlled by aggregation and sintering. The oxidation of silicon tetrachloride was assumed to be a first-order reaction when oxygen is excessive in the flame, while the hydrolysis of silicon tetrachloride was a second-order reaction. A particle-dynamic model of Kruis et al. (1993) was used. The rate equation of the oxidation can be expressed as

\[
\frac{dc}{dt} = -k_0 e^{-|E_c/RT|}c
\]  

When both the oxidation and hydrolysis reactions are considered, the overall rate equation can be expressed as

\[
\frac{dc}{dt} = -k_{s,0} e^{-|E_s/RT|}c_k e^{-|E_s/RT|}c
\]  

According to some published articles (Powers, 1978; Kochubei, 1997; Kim et al., 2005), \(E_s = 400.0 \text{ kJ/mol}, k_0 = 3.10 \times 10^{19} \text{ s}^{-1}, E_s, k_0 \) = 121.4 kJ/mol, and \(k_{s,0} e^{-|E_s/RT|}c_k e^{-|E_s/RT|}c = 1.00 \times 10^{12} \text{ s}^{-1}.

Aggregation and sintering equation

The particle-number concentration can be expressed as

\[
\frac{dN}{dt} = - \frac{dc}{dt} N_0 - \frac{1}{2} \beta N^2 \rho_g
\]  

The volume of an aggregate, \(v\), is only affected by coagulation,

\[
\frac{dv}{dt} = - \frac{1}{N} \frac{dN}{dt} v
\]  

The surface area of an aggregate, \(a\), which increases by coagulation and decreases by sintering (Koch and Friedlander, 1990), can be described as

\[
\frac{da}{dt} = - \frac{1}{N} \frac{dN}{dt} a - \frac{1}{\tau} (a - a_c)
\]  

The coagulation kernel \(\beta\) takes the following form (Seinfeld, 1986; Schaefer and Hurd, 1990; Schild et al., 1999):

\[
\beta = 8\pi Dr_c \left[ \frac{r_c}{2r_c + \sqrt{2}g} + \frac{\sqrt{2}D}{Cr_c} \right]^{-1}
\]  

The sintering time \(\tau\) in Equation (5) can be obtained by the following equation (Tsantrizos et al., 2001):

\[
\tau = 6.5 \times 10^{-15} d_p \exp \left( \frac{8.3 \times 10^4}{T} \left(1 - \frac{d_{p,\text{min}}}{d_p} \right) \right)
\]  

The mean diameter of a synthesized NP is \(d_p = 6v/a\).

Hydrodynamic Model

Governing equations

A commercial CFD software FLUENT was used to simulate the combustion flame. The FLUENT database (Hong et al., 2005a) for reaction kinetics was employed. The governing equations for a steady-state, laminar, and reacting 2D flow are listed below.

Continuity equation:

\[
\nabla (\rho \vec{U}) = 0
\]  

Momentum equation:

\[
\nabla (\rho \vec{U} \vec{U}) = -\nabla p + \nabla \vec{\tau} + \rho \vec{g}
\]  

Temperature equation:

\[
C_p \nabla (\rho \vec{U} T) = \nabla (\lambda \nabla T) + \sum_{i=1}^{N_g-1} R_i M_i \Delta H_i
\]  

Species equations:

\[
\nabla (\rho \vec{U} Y_i) = \nabla (\rho D_i \nabla Y_i) + \sum_{i=1}^{N_g-1} R_i M_i (i = 1 - N_g - 1)
\]  

The gas density is calculated based on the ideal-gas law.

Solution

The following boundary conditions are imposed: (1) at the inlet, all variables are set accordingly; (2) at the axial symmetry, the derivatives of all variables are set to zero; (3) at the wall, the temperature is given. The non-slip and non-penetration boundary conditions are assumed for all variables. A grid of 9000 nodes was used with uniform grid spacing in both directions.

Thermodynamic Model

Theory of chemical thermodynamics

The thermodynamic calculations based on minimizing the Gibbs energy were conducted to obtain the equilibrium compositions.

The Gibbs energy of a system can be expressed as

\[
G_T = \sum_{i=1}^{N_g} n_i \mu_i = \sum_{i=1}^{N_g} n_i \left( G_i^0 + RT \ln \alpha_i \right)
\]  

The gas-phase species are assumed to have unit activities, \(\alpha_i = \rho_i\). Regarding the coexistence of condensed phases, Equation (13) can be rewritten as:

\[
G_T = \sum_{i=1}^{N_g} n_{\rho i} \left[ \frac{G_i^0}{RT} + \ln \rho_i + \ln \left( \frac{n_{\rho i}}{N_0} \right) \right]
\]  

with constraining conditions,

\[
n_{\rho i} \geq 0
\]
Figure 2. TEM photographs of silica NPs synthesized at different LPG flow rates ($Q_{\text{air}} = 115$ L/h). (a) $Q_{\text{LPG}} = 1.2$ L/h, (b) $Q_{\text{LPG}} = 2.7$ L/h, (c) $Q_{\text{LPG}} = 3.9$ L/h, and (d) $Q_{\text{LPG}} = 6.0$ L/h.

The equilibrium compositions of the Si–Cl–N–H–C–O system can be calculated by minimizing Equation (13) with the constraining conditions, Equations (14) and (15). Details about the computer program can be found in our published articles (Hong et al., 1997, 2003).

**Elements and species**

The computed results could be erroneous if some important species were not included. On the other hand, if some species...
are assumed, which do not actually exist, their concentrations are taken to be zero, and the accuracy of the results will not be affected. Only the major component of LPG, \( \text{C}_4\text{H}_{10} \), was used in the thermodynamic and hydrodynamic simulations. It is assumed that there are 6 elements and 100 species in the system. The six elements are C, Cl, H, O, N, and Si. The 100 species are \( \text{N}_2, \text{HCl}, \text{CO}_2, \text{CO}, \text{H}_2, \text{H}_2\text{O}, \text{CH}_4, \text{NH}_3, \text{HCN}, \text{CH}_3\text{O}, \text{Cl}, \text{CHNO}, \text{HCO}, \) and more. The Gibbs energy \( (\Delta G) \) at different temperatures can be found in Barin et al. (1993).

## RESULTS AND DISCUSSION

### Influence of LPG Flow Rate

The variation of mean particle size and size distribution were investigated by fixing the air-flow rate at 115 L/h and the oil bath temperature at 293 K. The flow rate of LPG was increased gradually from 1.2 to 8.4 L/h with the air:fuel ratio decreasing from 95.8 to 13.7. Figure 2 shows the TEM photographs of synthesized silica NPs under different LPG flow rates. Figure 3 illustrates the effect of LPG flow rate on the mean diameter of silica NPs. The diameter of silica NPs was obtained from the TEM photographs. When the LPG flow rate increased gradually, flame height, flame temperature, and water content in combustion flame increased obviously. The flame temperature was measured as reported by Hong et al. (2005b). The increase of LPG flow rate also leads to the increase of the coagulation and sintering. Hence, the diameter of the synthesized silica NPs increases rapidly as the increasing LPG flow rate.

### Influence of Air-Flow Rate

The influence of air-flow rate on the size of silica NPs was investigated by fixing the LPG flow rate at 3.3 L/h and the oil bath temperature at 293 K. The air-flow rate increased from 90 to 180 L/h gradually. Figure 4 illustrates the TEM photographs of the obtained silica NPs. The influence of air-flow rate on the mean diameter of silica particles is shown in Figure 5. The mean diameter of silica NPs decreases with the increasing air-flow rate, which might be due to the reduction of residence time and dilution of reactants. When the air-flow rate increases, the flame height decreases and the flame temperature is almost the same according to experimental measurement. The particle coagulation decreases with the decreasing particle residence time in the flame. Moreover, the \( \text{SiCl}_4 \) and \( \text{SiO}_2 \) concentrations in the flame are possibly reduced (Mueller et al., 2004) with the increasing air-flow rate, leading to the reduction of particle size.

### Influence of Oil Bath Temperature

The influence of oil bath temperature on the size of synthesized NPs was investigated by fixing the air-flow rate at 115 L/h, and the LPG flow rate at 3.3 L/h. The oil bath temperature increased from 293 to 323 K gradually. Figure 6 illustrates TEM photographs of NPs. The influence of oil bath temperature on the mean diameter of NPs is shown in Figure 7. The volatility of silicon tetrachloride and the monomer concentration of the silica in flame increase as the oil bath temperature increases, which leads to the increase of the coagulation and sintering. Hence, the diameter of the synthesized NPs increases rapidly.

### Influence of Combustion Flame

The diameter of silica NPs is determined primarily by the flame temperature and the residence time of monomers/particles in the combustion flame. Our previous study showed that the diameter distribution strongly depends on the residence time distribution (Hong et al., 2005b). Figure 8 shows the flame shape at different flow rates recorded using a CCD camera in the experiments. From Figure 8 we can see that the flame is annular at low LPG flow rate, the residence times of the silica monomers/particles travelling upward through the centre or the edge of flame are different. In this case, particles with wide size distribution can be obtained. When the LPG flow rate increases, the flame shape is no longer annular, and the particles travelling upward through the centre or the edge of the flame have similar residence time. In this case, the particles with narrow size distribution can be obtained. From Figure 9 we can see the temperature distribution. In a typical case, the calculated height of a flame was about 200 mm, which was verified by experiment observation. Hence, the length of the flame was set to 200 mm in the particle-dynamic simulation.

Another interesting phenomenon revealed by hydrodynamic simulation is the existence of backflow region near the bottom of the flame. This phenomenon results in the distribution of particle residence time, which was ignored in the particle-dynamic simulation for simplicity.

### DSC-TG Analysis

Figure 10 is the DSC-TG curves of the synthesized products, which were obtained at the LPG flow rate of 3.3 L/h, the air-flow rate of 115 L/h, and the oil bath temperature at 293 K. The DSC-TG tests were performed under the protection of inert gas, and the temperature increase rate is 20 °C/min. It can be seen that there is a weight loss between room temperature and 180 °C, indicating the release of physically absorbed water. The weight loss at about 480 °C is attributed to the dehydration of Si–OH, and this loss is about 2.1%. The peak at 791 °C has only calorific capacity change, but the weight loss is not obvious as ascribed to the crystallization of silica.
Figure 4. TEM photographs of silica NPs synthesized at different air-flow rates ($Q_{LPG} = 3.3\text{L/h}$). (a) $Q_{air} = 90\text{ L/h}$, (b) $Q_{air} = 120\text{ L/h}$, (c) $Q_{air} = 140\text{ L/h}$, and (d) $Q_{air} = 180\text{ L/h}$.
about 480 and 48.63 which can be detected by the FT-IR, in other words, the Si(OH)$_4$ peak of Si(OH)$_4$ was weakened obviously, in accordance with the standard IR spectra of silica. Other weak peaks at 1635 and 3500 cm$^{-1}$ are, respectively, due to the bending vibration of water absorbed by silica and the asymmetrical stretching vibration of Si–OH. Because of the coexistence of the oxidation and hydrolysis reactions, the Si(OH)$_4$ formed due to the hydrolysis reaction and then decomposed to silica. There also existed some Si(OH)$_4$, which can be detected by the FT-IR, in other words, the Si(OH)$_4$ did not have enough time to decompose to silica as the flame was not long enough. When silica was heated at 600$^\circ$C for 3 h, the peak of Si(OH)$_4$ was weakened obviously, in accordance with the DSC-TG result that the decomposition temperature of Si(OH)$_4$ is about 480$^\circ$C.

FT-IR Analysis

Figure 11 is the FT-IR absorption spectrum of the products, synthesized at the LPG flow rates of 3.3 L/h, the air-flow rate of 115 L/h, and the oil bath temperature at 293 K. As shown in Figure 11, the peak at 1088 cm$^{-1}$ is due to the asymmetrical stretching vibration of Si–O–Si, and the peak 815 cm$^{-1}$ is due to the symmetrical stretching vibration of Si–O–Si. These results are in accordance with the standard IR spectra of silica. Other weak peaks at 1635 and 3500 cm$^{-1}$ are, respectively, due to the bending vibration of water absorbed by silica and the asymmetrical flex vibration of Si–OH. Because of the coexistence of the oxidation and hydrolysis reactions, the Si(OH)$_4$ formed due to the hydrolysis reaction and then decomposed to silica. There also existed some Si(OH)$_4$, which can be detected by the FT-IR, in other words, the Si(OH)$_4$ did not have enough time to decompose to silica as the flame was not long enough. When silica was heated at 600$^\circ$C for 3 h, the peak of Si(OH)$_4$ was weakened obviously, in accordance with the DSC-TG result that the decomposition temperature of Si(OH)$_4$ is about 480$^\circ$C.

XRD Analysis

Figure 12 shows the XRD spectra of the products obtained at the LPG flow rate of 3.3 L/h, the air-flow rate of 115 L/h, and the oil bath temperature of 293 K. The spectra show that the synthesized silica NPs are amorphous. A wide diffraction peak of 2$\theta$ = 23$^\circ$, which is the characteristic peak of amorphous silica, can be found. When the sample was heated at 300 or 600$^\circ$C for 3 h, the sample was still amorphous. When the sample was heated at 900$^\circ$C, there appeared the weak peaks at 2$\theta$ = 21.92$^\circ$, 28.44$^\circ$, 31.45$^\circ$, 36.10$^\circ$, and 48.63$^\circ$, which are corresponding to a series of characteristic peaks: 4.050 (1 0 1), 3.135 (1 1 1), 2.841 (1 0 2), 2.485 (2 0 0), and 1.870 (2 1 2) in the pattern of silica. The $d$ values calculated from the XRD patterns are well indexed to the cristobalite (International Center for Diffraction Data, JCPDS 11-695). These results indicate that the temperature for amorphous silica to crystallize is below 900$^\circ$C, and agree with those from DSC-TG analysis.

Predictions of Silica Diameter From Particle Dynamics

Competition between oxidation and hydrolysis reactions

In a typical case, the silicon tetrachloride inlet concentration was chosen as 0.005 mol/L, as will be discussed in Particle Size at Different Reaction Mechanism Section.

Figure 13 compares the formation rates of silica from oxidation and hydrolysis reactions at different reaction temperatures. The results are obtained at the silicon tetrachloride feed concentration of 0.005 mol/L and the oxygen concentration of 0.21. The oxidation and hydrolysis rates were calculated at the reaction temperature from 700 to 2200 K. We can see from Figure 13 that when the temperature is relatively low, the hydrolysis is much faster than the oxidation. Only when the temperature approaches 2000 K, the oxidation becomes faster than the hydrolysis.

Particle size at different reaction mechanism

When the air-flow rate is 115 L/h, the LPG flow rate is 3.3 L/h, and the oil bath temperature is 293 K, it can be calculated from the mass conservation and the saturated vapour pressure of SiCl$_4$ that the water concentration is 0.95 mol/m$^3$, and the feed concentration of silicon tetrachloride is 0.005 mol/L. It was measured in the experiment that the flame length is 20 cm, the reaction temperature is 1450 K, and the total air-flow rate is 0.2 m$^3$/s. Then the following cases are simulated in the numerical computations: instantaneous reaction, oxidation reaction, hydrolysis reaction, and oxidation plus hydrolysis reactions. The silica diameters predicted by various reaction mechanisms are illustrated in Figure 14. We found that the hydrolysis is the major factor determining the diameter of silica NPs. So the oxidation reaction can be ignored if the temperature is not too high.

Particle size versus reaction temperature

The feed concentration of silicon tetrachloride was kept at 0.005 mol/L, the air-flow rate at 0.20 m$^3$/s, and the water concentration at 0.95 mol/m$^3$, and the reaction temperature was set to be 1150, 1250, 1350, 1450, and 1550 K in turn. The silica particle diameter and silicon tetrachloride conversion at these reaction temperatures are illustrated in Figures 15 and 16, respectively. It could be found that the NPs diameter and silicon tetrachloride conversion increase with the increasing flame temperature when the flame length is fixed. From the simulation, we can conclude that the optimal reaction temperature is about 1400 K, which is in accordance with the thermodynamic calculations.

Particle size versus silicon tetrachloride feed concentration

The reaction temperature was set at 1450 K, the air-flow rate at 0.20 m$^3$/s, and the water content at 0.95 mol/m$^3$, and the feed concentration of silicon tetrachloride was set to be 0.0005, 0.001, 0.005, 0.01, and 0.05 mol/L in turn. The silica particle diameter and silicon tetrachloride conversion are shown in Figures 17 and 18, respectively. We can find that the silica NPs diameter increases while the conversion decreases with more silicon tetrachloride added. It is also found that the particle diameter increases with the increasing oil bath temperature, as shown in Figure 7, since the feed concentration of silicon tetrachloride also increases.

Particle size versus water concentration

The reaction temperature was set at 1450 K, the air-flow rate at 0.20 m$^3$/s, and the feed concentration of silicon tetrachloride at
Figure 6. TEM photographs of silica NPs synthesized at different oil bath temperature. (a) $T = 20^\circ C$, (b) $T = 30^\circ C$, (c) $T = 40^\circ C$, and (d) $T = 50^\circ C$.

0.005 mol/L, and the water concentration was set at 0.3, 0.5, 0.75, 0.95, 1.2, 1.6, and 2.0 mol/m$^3$ in turn. The silica particle diameter and silicon tetrachloride conversion versus water concentration are shown in Figures 19 and 20, respectively. It can be found that the reaction rate increases with the increasing water concentration.

Particle size versus total air-flow rate

The reaction temperature was fixed at 1450 K, the water concentration at 0.95 mol/m$^3$, and feed concentration of silicon tetrachloride at 0.005 mol/L, and the total air-flow rate was changed from 0.1 to 0.4 m$^3$/s with an interval of 0.14 m$^3$/s.
Mean particle size of silica at different oil bath temperature.

The silica particle diameter and silicon tetrachloride conversion at different axial locations are shown in Figures 21 and 22, respectively. It can be found that the diameter and the conversion decrease when the total air-flow rate increases. The reduction of particle size with the increasing air-flow rate is verified by the experimental result in Figure 5. The silica diameter and the silicon tetrachloride conversion increase in the flow direction through the flame. The higher the air-flow rate, the lower the particle residence time. As a result, both the particle diameter and conversion are reduced.

Thermodynamic Analysis

Influence of reaction temperature on equilibrium compositions

At atmospheric pressure, the mole ratio of the species is $O_2:N_2:C_4H_{10}:SiCl_4 = 20:80:4:5$, the temperature is changed from 1000 to 2000 K. The major gas components, according to their...
equilibrium concentrations, are CO₂, CO, H₂, and H₂O, as shown in Figure 23. It can be seen from the figure that the concentrations of gas species are influenced greatly by temperature. Apparently, the optimal temperature is between 1000 and 1500 K to reduce the concentration of CO. But the temperature should not be too low to reduce the reaction rates. The result agrees with the prediction of particle-dynamic model in Particle Size Versus Reaction Temperature Section.

**Influence of silicon tetrachloride on equilibrium compositions**

The mole ratio of silicon tetrachloride was increased from 1 to 9 in turn. The silicon tetrachloride mole ratio of 3 means: O₂:N₂:C₄H₁₀:SiCl₄ = 20:80:4:3. The temperature was set to be 1450 K. As shown in Figure 24, the concentration of CO increases while others decrease. Therefore, the mole ratio of silicon...
tetrachloride should be low. When the feed concentration of silicon tetrachloride is reduced, the output of the apparatus will also be lowered. So the optimal ratio of silicon tetrachloride is between 4 and 5.

After the thermal dynamic calculation, we adopted the optimal ratio of reactants in the experiments, as already discussed in Influence of LPG Flow Rate Section to Influence of Oil Bath Temperature Section.
Figure 20. Influence of water concentration on silica conversion.

Figure 21. Influence of total air-flow rate on silica diameter.

Figure 22. Influence of air-flow rate on silica conversion.

Figure 23. Influence of temperature on major equilibrium compositions.

Figure 24. Influence of SiCl₄ mole ratio on major equilibrium compositions.

Figure 25. Influence of C₄H₁₀ mole ratio on major equilibrium compositions.
Influence of LPG on equilibrium compositions

The mole ratio of C₄H₁₀ was increased from 2 to 8 in turn. The C₄H₁₀ mole ratio of 4 means: O₂:N₂:C₄H₁₀:SiCl₄ = 20:80:4:5. The temperature was set to be 1450 K. As shown in Figure 25, when the concentration of C₄H₁₀ increases, the concentrations of CO and H₂ increase quickly. That is due to the incomplete combustion of C₄H₁₀.

It is interesting to find that the highly toxic gas HCN generated in the combustion flame when the fuel is excess. When the mole ratio of C₄H₁₀ is 8, the mole ratio of HCN is 2.74 × 10⁻⁴. So the mole ratio of C₄H₁₀ should not be too high in the experiments.

CONCLUSIONS

Using silicon tetrachloride as a precursor, silica NPs were synthesized in the diffusion flames of air and LPG. A particle-dynamic model was used to study the nucleation, coagulation, and sintering during the generation of NPs. The particle sizes predicted by the particle dynamics agree with the experimental findings. The mean particle size of the synthesized NPs is about 25–30 nm in an optimal condition. Effects of air and LPG flow rates, flame shape on the synthesized NPs were investigated. The mean size of NPs increased with the increasing LPG flow rate and evaporator temperature. With the air-flow increasing, the mean particle size of silica decreased. The synthesized NPs are amorphous and start to crystallize when being heated at 900°C. A hydrodynamic model was used to simulate the diffusion flame of the experiment. From the simulation we can see some details of the flame, which were in accordance with the experimental results. Chemical thermodynamic simulation gave the equilibrium compositions, and the optimal temperature and ratio of reactants. From both the particle-dynamic and the thermodynamic analyses, we can conclude that the optimal temperature in the experiment is about 1450 K. Our presented models in this paper could be served as promising tools for laboratory research and industry design.

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NOTATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₀(j)</td>
<td>coefficient of element j in species i of phase ϕ</td>
</tr>
<tr>
<td>a</td>
<td>mean particle surface area (m²)</td>
</tr>
<tr>
<td>aₐ</td>
<td>surface area of a completely fused aggregate (m²)</td>
</tr>
<tr>
<td>Bᵢ</td>
<td>total mole number of element j in the system (mol)</td>
</tr>
<tr>
<td>C</td>
<td>particle velocity (m/s)</td>
</tr>
<tr>
<td>c</td>
<td>concentration of precursor (mol/m³)</td>
</tr>
<tr>
<td>C_p</td>
<td>heat capacity at constant pressure (J/kg K)</td>
</tr>
<tr>
<td>S_{SiCl₄}</td>
<td>silicon tetrachloride concentration (mol/m³)</td>
</tr>
<tr>
<td>D</td>
<td>particle diffusion coefficient</td>
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<td>D_l</td>
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<td>E_{H₂O}</td>
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<tr>
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</tr>
<tr>
<td>C_i^0</td>
<td>standard Gibbs energy of species i (J/mol)</td>
</tr>
<tr>
<td>T</td>
<td>unit tensor</td>
</tr>
<tr>
<td>i</td>
<td>denoting gas species i</td>
</tr>
<tr>
<td>g</td>
<td>transition parameter</td>
</tr>
<tr>
<td>g</td>
<td>gravitational acceleration (m/s²)</td>
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<tr>
<td>k_0</td>
<td>pre-exponential factor of the oxidation (s⁻¹)</td>
</tr>
<tr>
<td>k_{H₂O}</td>
<td>pre-exponential factor of the hydrolysis (s⁻¹)</td>
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<td>l</td>
<td>length of the entrance of the reactor (mm)</td>
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<tr>
<td>m</td>
<td>denoting surface species (m)</td>
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<tr>
<td>m_ϕ</td>
<td>number of species in phase ϕ</td>
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<tr>
<td>M_k</td>
<td>molecular weight of gas species k (g/mol)</td>
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<tr>
<td>N</td>
<td>particle-number concentration in particle-dynamic computation (m⁻³)</td>
</tr>
<tr>
<td>N_T</td>
<td>total species in thermodynamic computation</td>
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<tr>
<td>N_A</td>
<td>the Avogadro constant</td>
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<tr>
<td>N_g</td>
<td>total number of gas-phase species</td>
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<tr>
<td>n_ϕ</td>
<td>mole number of phase ϕ (mol)</td>
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<td>n_ϕ,i</td>
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<tr>
<td>n_i</td>
<td>mole number of species i (mol)</td>
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<tr>
<td>p</td>
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<tr>
<td>p_i</td>
<td>partial pressure of species i (Pa)</td>
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<tr>
<td>Q</td>
<td>gas flow rate (m³/s)</td>
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<tr>
<td>q</td>
<td>number of species in condensed phase</td>
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<tr>
<td>R</td>
<td>gas constant (J/mol K)</td>
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<td>R_o</td>
<td>radius of the inner tube of the reactor (mm)</td>
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<tr>
<td>R_out</td>
<td>radius of the outer tube of the reactor (mm)</td>
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<tr>
<td>r_c</td>
<td>mean aggregate radius (or collision radius) (m)</td>
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<tr>
<td>r_p</td>
<td>primary particle radius (radius of silica monomer) (m)</td>
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<tr>
<td>s</td>
<td>number of species in solid phase</td>
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<td>s_m</td>
<td>molar production rate of the mth surface species (mol/m² s)</td>
</tr>
<tr>
<td>T</td>
<td>temperature (K)</td>
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<tr>
<td>U</td>
<td>velocity vector (m/s)</td>
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<tr>
<td>ν</td>
<td>mean solid volume (m³)</td>
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<tr>
<td>W_{m}</td>
<td>mixture average molecular weight (g/mol)</td>
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<tr>
<td>Y_k</td>
<td>weight fraction of species k</td>
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</table>

Greek Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>α_i</td>
<td>activity of species i</td>
</tr>
<tr>
<td>β</td>
<td>coagulation kernel</td>
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<tr>
<td>ϕ</td>
<td>denotes respective phase</td>
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<tr>
<td>λ</td>
<td>thermal conductivity (cal/m K s)</td>
</tr>
<tr>
<td>ρ</td>
<td>density of gas mixture (g/cm³)</td>
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<tr>
<td>μ</td>
<td>viscosity of gas mixture (g/cm² s)</td>
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<tr>
<td>ΔH_k</td>
<td>heat of reaction for species k (cal/mol)</td>
</tr>
<tr>
<td>τ</td>
<td>characteristic sintering time (s)</td>
</tr>
<tr>
<td>η</td>
<td>viscous stress tensor (Pa)</td>
</tr>
<tr>
<td>μ_s</td>
<td>chemical potential of species i</td>
</tr>
</tbody>
</table>

Subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<td>k</td>
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<tr>
<td>g</td>
<td>gas-phase reactions</td>
</tr>
<tr>
<td>s</td>
<td>surface reactions</td>
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REFERENCES


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