Effects of charge and size on condensation of supersaturated water vapor on nanoparticles of SiO₂

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The effects of size and charge on the condensation of a supersaturated water vapor on monodisperse nanoparticles of SiO₂ were investigated in a flow cloud chamber. The dependences of the critical supersaturation S_{cr} on particle size at diameters of 10, 12, and 15 nm as well as on charge and charge polarity are determined experimentally. A novel electrospray aerosol generator was developed to generate a high concentration of SiO₂ nanoparticles of less than 10 nm by electrospraying silicon tetraethoxide (STE) ethanol solution followed by the thermal decomposition of STE. The effects of liquid flow rate, liquid concentration, flow rate of carrier gas, and liquid conductivity on the particle size distribution and concentration were examined. For charged particles, the nucleation occurs at a critical supersaturation S_{cr} lower than that on neutral particles, and the charge effect fades away as particle size increases. The charge effect is stronger than the theoretical predictions. In addition, a sign preference is detected, i.e., water vapor condenses more readily on negatively charged particles, a trend consistent with those observed on ions. However, both effects of charge and charge polarity on S_{cr} are stronger than that predicted by Volmer’s theory for ion-induced nucleation.

I. INTRODUCTION

Various fine aerosols are generated as a result of certain natural and anthropogenic activities. Over land, there are about 10 ion pairs cm⁻³ s⁻¹ formed by the action of cosmic radiation and radioactive gases emanating from the soil. These ions attach to aerosol particles, leading to the formation of charged particles and reaching Boltzmann equilibrium charge distribution in 100 min. Condensation of supersaturated vapor on neutral insoluble particles is influenced by the surface properties and size of the particles. Condensation of a vapor onto charged particles is further influenced by the sign and the amount of charge and the dipole moment of the vapor molecules. Ions are believed to interact with the condensing vapor and change the energy barrier for nucleation. So far, the size of the ions tested ranges from single atoms or small molecules consisting of a few atoms to macromolecules containing hundreds of atoms. For small ions with diameters less than 1 nm, there is no reported dependence of the nucleation rate on the size and the chemical makeup; but, for macromolecules with diameters of about 1 nm, a decrease in the critical supersaturation with ion size is observed. In a previous study for the condensation of supersaturated water vapor on SiO₂ and TiO₂ nanoparticles of a diameter of 30–90 nm, there is no obvious effect of charge on S_{cr} observed, in agreement with the theoretical prediction. However, only scant data are available for the condensation of vapor onto charged particles with diameters in the range of tens or less of nanometers.

In our earlier studies, systematic studies were performed aiming at gaining more insights into the heterogeneous nucleation process. For most tested particles, we observed a smaller S_{cr} than that for perfectly wetted insoluble particles and a dependence of S_{cr} on size and temperature qualitatively consistent with that predicted by the Fletcher version of Volmer theory of heterogeneous nucleation. However, to make the experimental S_{cr} agree with the theory, a smaller surface tension of the condensing vapor was required, i.e., 20% (or less) and 80% of the bulk surface tension for n-butanol and water, respectively. So far no model is available to give a satisfactory explanation consistent with the observations quantitatively. More studies are needed.

To foster our knowledge about the sign preference as well as the effects of charge and size of particle on the S_{cr}, in the present study, the condensation of water vapor onto monodisperse SiO₂ particles with diameters of 10, 12, and 15 nm, each carrying a single positive charge, a single negative charge, or no charge, was carried out. A novel nanoparticle generator employing electrospraying method was developed to produce a stable, high concentration, and narrow-sized distribution SiO₂ aerosols to supply suitable amount of nanoparticles of a diameter of about 10 nm to make the study possible. The operation characteristic of the generator, including variations of the concentration and particle size as functions of flow rates of gas and liquid and concentration of reactant, was studied. The effects of charge, charge polarity, and size on the S_{cr} were examined and compared with the predictions of the classical ion-nucleation theory.

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II. EXPERIMENT

A. Experimental setup

The experimental apparatus is illustrated in Fig. 1. A syringe pump supplies the silicon tetraethoxide [STE, Si(OCH₃)₄] ethanol solution to an electrosprayer where submicrometer droplets are electrosprayed in a cone-jet mode. Clean air carries the droplets out of the electrosprayer. The air-reactant stream is mixed with a second air stream and enters the oven. The polydisperse aerosol generated in the oven passes through an electrostatic classifier (model 3071A, TSI) to produce a singly positively/negatively charged monodisperse aerosol. The charged monodisperse particles enter an aerosol neutralizer (model 3077, TSI) to reach charge equilibrium. The charged particles are removed by an electrostatic collector. The uncharged monodisperse aerosol is diluted with clean air and then flows through the flow cloud chamber (FCC) where a supersaturated vapor is created and the degree of supersaturation is increased by increasing temperature gradient between the chamber’s plates. The removal efficiency is obtained by comparing particle concentrations at the inlet and the outlet of the FCC. The particle concentration is measured using an ultrafine condensation particle counter (model 3025A, TSI). In experiments that measure the charge effect, the aerosol neutralizer and the electrostatic collector are not used. The charged particles from the classifier are diluted with clean air and enter the FCC directly as indicated by the dashed line. The polydisperse aerosol is generated by the thermal decomposition of STE vapor in the oven at 800 °C via the reaction

\[
\text{Si(OCH}_3\text{)}_4 + 12\text{O}_2 \rightarrow \text{SiO}_2 + 8\text{CO}_2 + 10\text{H}_2\text{O}
\]

The entire experimental setup except for the electrospray system is similar to that has been used in previous studies,⁴⁻⁵ and most equipments and instruments mentioned above have also been previously employed and explained elsewhere.⁴⁻¹⁰ Only a brief description of the equipment specific or important to the current study is given here.

1. Aerosol generators

Recently nanoparticles have attracted extensive studies. The small size of nanoparticles makes them have different properties such as electronic, optical, magnetic, mechanical, electric, chemical, etc., with respect to the bulk materials and suitable for new applications.¹¹ Various methods have been developed to synthesize nanoparticles including sol-gel process, gas-phase process, etc., where gas-phase processing system may be better in some cases because of their inherent advantages. Among the various gas-phase processing methods, an electrospray system has been shown to yield small droplets with a narrow size distribution when operated in the cone-jet mode,¹² and then leading to the production of nanoparticles with narrow size distribution. In the study an electrospray aerosol generator was developed to generate SiO₂ nanoparticles by electrospraying silicon tetraethoxide (STE) ethanol solution in cone-jet mode followed by the thermal decomposition of STE.

Figure 2 shows a diagram of the electrosprayer. It consists of an electrospraying chamber, a corona discharging chamber, and a mixing chamber. A syringe pump supplies the STE ethanol solution through a capillary tube into the electrospraying chamber where micrometer droplets are electrosprayed from the tip of the capillary tube in a cone-jet mode. Clean air carries the droplets out of the electrospraying chamber.
chamber. The air-reactant stream is mixed with a second air stream from the corona discharging chamber to adjust the charge of the droplets and enters the oven to produce a polydisperse SiO$_2$ aerosol via the thermal decomposition of STE, Si(OCH$_3$)$_4$, vapor in the oven at 800 °C. The use of a corona discharging stream is to reduce the number of charges carried by each charged droplet to minimize their loss by charge dispersion force during their transport. The conductivity of the STE solution is adjusted by dissolving a small amount of ammonium acetate, and the STE vapor concentration was controlled by its liquid concentration and the total flow rate of carrier and corona discharging air streams. Since the use of the corona discharging air stream also leads to a dilution of the STE vapor concentration, hereafter, it is called diluting stream. The size distribution is analyzed by a scanning mobility particle sizer (SMPS, model 3934, TSI) operated in a polydisperse aerosol flow rate at 0.8 l/min, where aerosols enter an electrostatic classifier (model 3071A, TSI), classifying the polydisperse aerosol into a monodisperse aerosol whose concentration was counted by an ultrasonic condensation particle counter (UCPC, TSI 3025A). The effects of the liquid flow rate, the STE concentration, the flow rate of carrier gas, and the liquid conductivity on the particle size distribution and concentration were examined. The morphology of the particles, analyzed by x-ray diffraction (XRD), shows that the SiO$_2$ is amorphous.\textsuperscript{10}

2. Electrostatic classifier

The commercially available electrostatic classifier (model 3071A, TSI) employed in the study classifies polydisperse aerosol into monodisperse aerosol using a differential mobility analyzer (DMA). The DMA consists of a coaxial rod inside an electric-grounded cylindrical tube. An electric potential is applied to the central rod to create an electric field. As polydisperse aerosol passes through the annular space in a laminar flow, charged particles with a certain size were attracted to an exit in the bottom of the central rod and output as a charged monodisperse aerosol. The charge polarity of the aerosol is in opposition to the polarity applied to the central rod. In order to study the sign preference in the heterogeneous nucleation on charged nanoparticles, the classifier was modified to use an external bipolar power supplier to apply the potential to the central rod so that we can switch the polarity to generate positively or negatively charged particles.

B. Measurement of removal efficiency

Blank runs were first carried out for each aerosol stream to serve as a baseline for comparison with experiments where removal by nucleation is important. For the blank runs, the top and the bottom plates of the FCC were kept wet and set to the same temperature. In the removal runs the temperature of the top plate was held at a higher temperature to create a supersaturated vapor whose degree of supersaturation increases with the temperature gradient. The removal efficiency was measured as a function of supersaturation for SiO$_2$ particles of diameters of 10, 12, and 15 nm, each carrying a single positive or negative charge or no charge. The experimental procedure has been described in detail elsewhere.\textsuperscript{8,9} Only a brief description of the experiments and the operating condition are given. In the present study, a steady flow of 2 l/min of gas through the FCC was established, and the particle concentrations entering and exiting the FCC were recorded over a 6 min period. To minimize the uncertainty in determining the critical supersaturation, a 7 mW He–Ne laser (beam diameter of 0.8 mm) was used to illuminate the FCC at a few millimeters above the bottom surface to detect light scattered by the falling droplets produced as a result of nucleation. The location (distance from the entrance) where nucleation occurred and the number of droplets were recorded. These observations, together with the rapid change in particle removal efficiency with supersaturation, enable us to determine the supersaturation at which nucleation occurs.

For the blank runs, the top and the bottom plates of the FCC were kept wet and set at the same temperature of 294 K. In the removal runs, the bottom plate was set at a temperature of about 294 K, and the temperature of the top plate was set at temperature from 2 to 29 K higher. The maximum value of the supersaturation profile studied, $S_m$, and the corresponding temperature, $T_m$, at the position where peak supersaturation occurs are listed in Table I.

Note that the temperatures listed in the Table I indicate the mean value only. As has been described in a previous study,\textsuperscript{7} there is an uncertainty of about ±0.03 °C in the temperature.
terature measurements, which results in an uncertainty in the calculated values of $S_m$ whose value increases with the temperature gradient, e.g., uncertainties of $\pm0.0004$, $\pm0.0012$, and $\pm0.0015$ at $S_m$ of 1.0151, 1.1436, and 1.243, respectively.

III. COMPUTATION OF THE THEORETICAL CRITICAL SUPERSATURATION

Certain particles within the gas stream passing through the FCC nucleate supersaturated vapor, grow to larger sizes, and settle out with appreciable velocities. Before the particles fall onto the surface of liquid pool and are trapped, they travel with gas stream. Particles with a traveling distance less than the length of FCC are removed. Meanwhile, certain particles may also be trapped on surfaces when they move to surfaces due to Brownian motion, mass sweeping diffusion, and charge dispersion. The evaluation of the efficiency has been explained in detail in our previous studies, and the result shows that, as supersaturation increases, the efficiency increases sharply once the supersaturation passes a critical value, hereafter referred as the critical supersaturation $S_{cr}$, and approaches a value of 100%. This is the standard procedure to determine the theoretical $S_{cr}$.

Meanwhile, there are also two other simpler procedures, i.e., an iteration procedure and a constant temperature procedure, developed to evaluate the theoretical $S_{cr}$ from the nucleation rate equation describing the nonlinear dependence of nucleation rate on temperature and supersaturation [e.g., Eq. (5) along with Eqs. (1), (3), and (6), which will be shown later] corresponding to a nucleation rate of 1 nucleation event/particle s$^{-1}$. In the iteration procedure, the following scheme was used for each size of particles: (1) assume a temperature $T_s$ and solve for a $S_{cr}$, (2) interpolate a new $T_s$, corresponding to the $S_{cr}$ from Table I where the peak supersaturation occurs, listed for each temperature settings of the top and bottom plate, (3) reevaluate $S_{cr}$ at the new $T_s$, and (4) repeat steps (2) and (3) until the solution converges; while in the constant temperature procedure, a temperature $T_s$ was assumed and a $S_{cr}$ was solved for. As shown in Ref. 4, the theoretical $S_{cr}$ determined using the standard procedure agrees well with the theoretical $S_{cr}$ evaluated using the iteration procedure, agreeing to within 0.1% while the theoretical $S_{cr}$ evaluated using the constant temperature procedure also agrees well with the theoretical $S_{cr}$ evaluated using the iteration procedure, agreeing to within 0.2% or 0.6% depending on the value of $T_s$ used in two procedures, and the error increases with the difference between two $T_s$'s. It was found that for each size of particle the final value of $T_s$ obtained from the iteration procedure is very close to the value of experimental $T_s$ (the temperature at which the experimental critical supersaturation occurs). This is so because during iteration the value of $T_s$ is interpolated from the list of the variation of the peak supersaturation and the temperature at which peak supersaturation occurs with the temperatures of the plates (i.e., Table I). Therefore, one can obtain a minimum error in the prediction of theoretical $S_{cr}$ by the constant temperature procedure if the temperature corresponding to experimental critical supersaturation is used. In the present study, the critical supersaturation is evaluated using the constant temperature procedure at a $T_s$ of 303.15 K which is about the average of the temperatures at which the experimental critical supersaturations occur in all measurements.

A. The nucleation theories

In the study, Fletcher’s theory$^{13}$ was used to calculate the nucleation rate initiated by neutral particles. For charged particles, the ion interacts with the condensing vapor and lowers the energy barrier to nucleation. Such a charge effect has been taken into account by various theories in the evaluation of the change of Gibbs energy accompanying the formation of a critical embryo on an ion or a charged particle, $\Delta G^*$. Volmer$^{15}$ gives an equation to calculate $\Delta G^*$, which cannot predict the sign effect of the charge experimentally observed. Recently, Talanquer and Oxtoby$^{18}$ and Kusaka et al.$^{19,20}$ have applied a density functional theory to ion-induced nucleation; their theories also successfully predict the sign effect. Although the latter theories$^{17-20}$ are successful in predicting the sign effect, the theories are only semi-quantitative, as noted by their authors, unless accurate parameters are available. These theories are not ready to use in our study yet. In the study, Volmer’s theory for ion-induced nucleation was used. However, in addition to treat the charged particle as a perfectly wetted spherical ion of a radius $R_0$ with an electric charge located at the center of the particle as in a previous study,$^4$ we also consider the second case that the electric charge is assumed to be located on particle surface.

In the case of a charged particle treated as a perfectly wetted spherical ion of a radius $R_0$ with the electric charge located at the center of the particle as shown in Figs. 3(a) and 3(b), the change in Gibbs free energy required to form a critical embryo, $\Delta G^*$, is written as

$$\Delta G^* = -\frac{4\pi \rho_i}{3M}RT \ln S(r_1^2 - r_i^2) + 4\pi \rho_i (r_2^2 - r_i^2)$$

$$+ \frac{q^2}{2}(\kappa_0 - 1 - \frac{1}{r_i} - \frac{1}{r_i})$$

Here $\gamma$ is the surface tension of water, $\kappa_0$ and $\kappa$ are the dielectric constants of air and water, $q$ is the electronic charge in Gaussian units, $r_i$ is the radius that the charged particle has when it is in stable equilibrium with the vapor, and $r_k$ and $r_a$ are the largest and the next smaller roots of $\partial \Delta G / \partial r = 0$:

$$\frac{\rho_i}{M}RT \ln S - \frac{2\gamma}{r} \frac{(r^2 - r_i^2)}{r^2} \frac{\partial \gamma}{\partial r} + \frac{q^2}{8\pi \rho_i^2}(\kappa_0 - 1) = 0.$$  

To evaluate $\Delta G^*$, $r_i$ is set to $R_0$ if $r_a < R_0$ and is set to $r_k$ if $r_a > R_0$. For a given vapor pressure, a cluster of radius $r_c$ is in stable equilibrium with the vapor, and any ion or charged particle with a radius $R_0$ smaller than $r_c$ will spontaneously grow up to $r_c$.

However, for the case of assuming the electric charge to locate on particle surface as shown in Figs. 3(c) and 3(d),
there are more condensing water molecules strongly interacting with the charge compared to that shown in Figs. 3(a) and 3(b) due to the shorter interdistance between the charge and water molecules, leading to more lowering of the energy barrier. Equations (1) and (2) have to be modified to take into account the new circumstance. Furthermore, the shape of the embryo may also vary with the amount of condensate as depicted by Figs. 3(e) and 3(f) and the charge may shift to a location more stable and having lower Gibbs free energy, both leading to an accurate evaluation of the charge effect becoming very complicated if not impossible. For simplicity, the embryo is assumed to be a spherical cap on the particle and the charge locates at the center as shown in Fig. 3(d), and we proposed a simplified modification as follows:

\[
\Delta G^* = \frac{4\pi\rho_l RT}{3M} \ln S - \frac{2\gamma}{r} - \frac{(r^2 - r_i^2)}{r^2} \frac{\partial \gamma}{\partial r} + V_q \frac{q^2}{8\pi r^4} (\kappa_0^{-1} - \kappa_i^{-1}) = 0,
\]

(4)

where \( r_i \) is the radius of an ion which is assumed to be a water molecule for the present case and \( V_q \) is a factor to take into account the effect due to the exclusion of the embryo volume by the particle. The more the embryo volume excluded, the less the number of water molecules subjected to the charge interaction. And the ratio of embryo volume excluded by the particle varies with embryo size; consequently, the value of \( V_q \) changes accordingly. For an embryo growing to a radius equal to the diameter of the particle, the volume excluded by the particle is less than a half of the embryo as shown by the dashed line in Fig. 3(g); thus, a value of 0.5 for \( V_q \) can be regarded as the lower limit, while for a very large embryo, the embryo volume excluded by the particle becomes negligible and \( V_q \) approaches 1. In the study, the critical embryo at the critical supersaturation corresponding to each tested particle, calculated either by Volmer theory for ion nucleation or by the Fletcher version of heterogeneous nucleation theory, is larger than the particle; thus, it is a reasonable approximation to use a value of 0.5–1 for \( V_q \) for the estimation of the charge effect. However, it is imperative to note that the accuracy of the approximation depends on the actual shape of the embryo and charge location, and there is no information available for the evaluation of an accurate charge effect yet. Further study is needed.

B. Evaluation of the theoretical \( S_{ox} \)

For an insoluble spherical particle the nucleation rate \( J \) (i.e., the number of critical embryos created on its surface per unit time) is written as

\[ J = 4\pi r_o^2 K \exp \left( -\frac{\Delta G^*}{RT} \right), \]

(5)

where \( r_o \) is the particle radius, \( \Delta G^* \) is the critical Gibbs-free energy change accompanying the formation of a critical embryo on the particle surface, and \( K \) is a kinetic prefactor. When the growth of the embryo is assumed to be as a result of direct condensation of water molecules from vapor phase, \( K \) is then written as

\[ K = v_o A_i^* N_{as}, \]

(6)

where \( v_o \) is the collision frequency of vapor molecules on an embryo of unit surface, \( A_i^* \) is the area of the liquid-vapor interface between the embryo and vapor phase, and \( N_{as} \) is number of adsorbed water molecules on the particle surface per unit area. The theoretical \( S_{ox} \) is iteratively solved from the nonlinear equation describing the nucleation rate as a function of supersaturation, i.e., Eq. (5).

IV. RESULTS AND DISCUSSION

A. Aerosol generation by electrospray system

Figure 4 shows a typical size distributions analyzed by the SMPS for the aerosols generated by the electrospray system; it shows that the particle concentration increases with...
increasing size, reaches a maximum, and then decreases. The peak concentration and the diameter at which peak concentration occurs, hereafter called peak diameter, vary with the flow rates of liquid and gas stream as well as the liquid concentration and conductivity. Figure 5 shows that above a threshold value both peak concentration and peak diameter increase linearly with liquid flow rate. Similar variation is observed in the peak concentration and diameter as a function of the STE liquid concentration. Figure 6 shows that on increasing flow rate of the carrier gas stream, there exists an optimum rate for the peak concentration and the peak diameter, and similar variation is obtained for the diluting gas stream. The increase of liquid conductivity leads to a decrease of peak concentration and diameter, as shown in Fig. 7. The above variations of the peak concentration and the peak diameter with operation parameters are a result of (i) the variation of amount of STE available for the formation of SiO₂ particles and the subsequent growth and (ii) the effect of the dilution by gas streams.

In addition, it is found that the increase of the flow rate of the liquid leads to a wider range of voltage between the upper and the lower limits at which a stable cone-jet mode spraying can be maintained. In summary, the electrospray system we developed has succeeded in producing SiO₂ nanoparticles of less than 10 nm. The particle size distribution is controllable by the adjustment of the operation parameters such as flow rates, reactant concentration, etc. In general, both peak concentration and peak diameter increase with liquid flow rate and concentration but decrease with liquid conductivity. There exists an optimum gas flow rate to achieve a maximum peak concentration. Furthermore, the monodisperse SiO₂ aerosol exiting from the classifier was collected and examined by transmission electron microscope (TEM): it is confirmed that monodisperse aerosol has a very narrow size distribution as shown in the Fig. 8 for a TEM image of 15 nm particles. The picture also shows that the particles are spherical in shape.

B. Blank test

During the blank tests, particles are removed by sedimentation and adhesion onto surfaces due to diffusion, inertial impingement, or charge dispersion. As shown in Fig. 9, the ratio of concentration at the outlet to the inlet increases with the particle diameter. Since the efficiency of removal is equal to 1 minus the ratio, the result indicates that the efficiency decreases with increasing particle size. For particles of a diameter smaller than 0.2 μm, particle loss by sedimentation is negligible. Therefore, particles are primarily removed by adhesion onto surfaces due to diffusion or charge dispersion. Furthermore, it is interesting to note that positively charged particles suffer more loss than neutral and negatively charged particles. If the extra loss for positively charged particles is due to charge dispersion, then it should also be observed for the negatively charged particles. No satisfactory explanation can be given yet.
C. Removal runs

During the removal runs, more particles were removed because nucleation and particle growth induced sedimentation. Figure 10 illustrates the variation of the removal efficiencies as a function of supersaturation for negatively charged SiO$_2$ particles at diameters of 10, 12, and 15 nm, respectively, and similar variations were obtained for neutral and positively charged particles. The efficiency first increases slowly with increasing supersaturation. As the supersaturation reaches a certain value, the efficiency increases at a higher rate. At even higher supersaturation, no particles were detected at the exit. The fluctuations of efficiency are primarily due to the larger uncertainties indicated by the error bars, i.e., one standard deviation from the mean, which decrease from about ±10% at low efficiency to about ±1% at high efficiency. For clarity error bars are only included for one curve. As the particle size decreases, both the supersaturation at which removal efficiency increases faster and the supersaturation approaching 100% removal efficiency shift to larger value, qualitatively agreeing with the theoretical expectations.

D. Comparison of the experimental and theoretical critical supersaturations

The experimental $S_{cr}$’s are determined from the experimental removal efficiency curves (as shown in Fig. 10) together with observations of the laser light scattered by the falling droplets. The latter helps identify the probable range of experimental $S_{cr}$ and is crucial when the experimental removal efficiency curves are not sharp. The experimental $S_{cr}$ is identified as the supersaturation at which the experimental removal efficiency increases sharply and 1 droplet/s is observed at an inlet particle concentration of 250 particles/cm$^3$. Note that the observed rate of droplets is proportional to the inlet particle concentration: the observed rate is normalized to a rate one would observe at an inlet particle concentration of 250 particles/cm$^3$ so as to have a common basis for the comparison of droplet rate. A typical example illustrating how $S_{cr}$ is determined was published in the previous study. Since the number of data points, the measurement of the temperature, and the use of physical properties all affect the values of $S_{cr}$, some uncertainty is imposed on $S_{cr}$. The uncertainty interval of the $S_{cr}$ was so determined that the supersaturations cover an observed rate from 0.1 to about 3 droplets/s, and the resultant intervals are larger than those possibly contributed by all other factors such as temperature measurements and physical properties. The uncertainty interval is indicated by the error bar.

The theoretical $S_{cr}$’s for perfectly wetted particles corresponding to a nucleation rate of 1 nucleation event/particle s are evaluated at a constant temperature of 303.15 K. For neutral particles the Fletcher version of the Volmer theory of heterogeneous nucleation is used, while for charged particles the Volmer theory for ion nucleation is employed and...
two cases, i.e., the charge located at the center of the particle or on the surface of the particle, are considered.

The experimental values of $S_{cr}$ and $T_s$ (the temperature at the peak supersaturation) required to induce heterogeneous nucleation of water vapor on SiO$_2$ aerosols are summarized in Table II and are compared to theoretical predictions in Fig. 11. Data points indicate the experimental values of $S_{cr}$ for SiO$_2$ aerosols with diameters from 10 to 15 nm.

The top dashed curve indicates the theoretical $S_{cr}$'s evaluated by the Kelvin equation for perfectly wetted particles as a function of diameter. The second curve is an overlapping of two curves, one corresponds to the theoretical $S_{cr}$ evaluated using Fletcher version of Volmer theory for neutral particles and the other is evaluated using Volmer theory of ion nucleation for charged particles with the charge located at the center of particle. The overlapping of two curves indicates that there is no charge effect for the particle sizes tested when the charge is assumed to locate at the center of the particle.

Also shown in Fig. 11 are two broken curves indicated by $V_q$=0.5 and 1 for the theoretical $S_{cr}$ evaluated by the Volmer theory of ion nucleation for charged particles, assuming that the charge is located on particle surface: the upper one corresponds to a half sphere of the condensate in the embryo subjected to the charge interaction and the lower one corresponds to the entire embryo being made of the condensate and subjected to the charge interaction, respectively. The lower curve represents the maximum charge effect theoretically attainable.

For SiO$_2$ neutral aerosols, the experimental values of $S_{cr}$ agree well with the predictions by the Kelvin equation and are slightly higher than those predicted by the Fletcher version of the Volmer theory for perfectly wetted neutral particles. Within the framework of a macroscopic theory of heterogeneous nucleation, the results suggest that SiO$_2$ aerosols induce heterogeneous nucleation with an efficiency less than perfectly wetted particles; in the meantime, the increase of the experimental $S_{cr}$ with decreasing particle size shown in Fig. 11 agrees reasonably with the theoretical prediction.

However, our observation of a higher $S_{cr}$ than the prediction for neutral particles of a diameter of 10–15 nm is inconsistent with our previous observations$^{5–10}$ for particles of a diameter of 15–90 nm and those of Koutsy et al.$^{23}$ where a lower $S_{cr}$ than the prediction is observed. Figure 12 shows a summary of the size dependence of $S_{cr}$ obtained in the present study and the previous study.$^4$ Note that, for the 15 nm diameter SiO$_2$ aerosol, the experimental $S_{cr}$ observed in the present study is slightly higher than that observed in the earlier study.$^4$ This discrepancy may be due to the temperature dependence of the critical supersaturation. According to Fletcher’s version of nucleation theory, the critical

![FIG. 11. Summary of the variation in the $S_{cr}$ as a function of particle diameter. The circle, square, and triangle data points indicate particles each carrying a single positive charge, a single negative charge, or no charge, respectively. Error bars on the data points correspond to one standard deviation from the mean. From top to bottom, curve 1 represents the theoretical $S_{cr}$ evaluated by the Kelvin equation, and the overlapping lines, curves 2 and 3, indicate the theoretical $S_{cr}$ evaluated by (i) the Fletcher version of the Volmer theory for perfectly wetted and insoluble neutral particles and (ii) the nucleation theory for charged particle assuming that the charge is located at the particle center, respectively. Curves 4 and 5 correspond to that evaluated by the nucleation theory for charged particles assuming that the charge is located on particle surface with a half volume ($V_q$=0.5) and entire volume ($V_q$=1) of the embryo subjected to the charge effect, respectively. Each curve is evaluated at a temperature of 303.15 K.](image-url)
supersaturation increases with decreasing temperature and the dependence has also been experimentally confirmed in our previous study, where it was found that the experimental $S_{cr}$ increased with decreasing temperature but at a higher rate than the theory predicted.\textsuperscript{4} In the present study the temperature at bottom plate is 9 K lower than in the previous study (i.e., 294 K versus 303 K); as a result, the temperature in the nucleation zone is lower than in the previous study, thus lading to a higher $S_{cr}$\textsuperscript{24}.

In summary, the results in Fig. 12 indicate that, qualitatively, the nucleation ability of neutral SiO$_2$ aerosols is consistent with the theoretical prediction, but, quantitatively, the experimental $S_{cr}$ is slightly higher than the value predicted by Fletcher’s theory for perfectly wetted particles.

E. Charge effect on the critical supersaturation

As shown in Fig. 11, the charged particles of SiO$_2$ with diameters of 10, 12, and 15 nm, each carrying a single positive or negative charge, have lower experimental $S_{cr}$ than neutral particles with a difference in $S_{cr}$ larger than the experimental uncertainty, thus revealing an obvious effect of charge on $S_{cr}$. This observation is inconsistent with the predictions of the classical ion-nucleation theory\textsuperscript{4,15,16,25} assuming that the charges is located at the center of particle, by which no charge effect for particles of a diameter larger than 4 nm is expected as shown in Fig. 11 by the two overlapping curves. The theory predicts that for a particle of a diameter less than 0.8 nm, the critical supersaturation required to induce a nucleation rate of 1 embryo/particle s for perfectly wetted charged particles remains a constant with a value much smaller than that of neutral particles. As the particle size increases, the $S_{cr}$ decreases, approaches to the $S_{cr}$ for neutral particles (e.g., at a diameter of 2 nm, a $S_{cr}$ of 2.10 for charged particle compared to a $S_{cr}$ of 2.17 for neutral particles), and becomes essentially the same at a diameter of 4 nm.

However, when the charge is assumed to locate on the surface of the particle, an obvious lowering in $S_{cr}$ is predicted for charged particles in comparison with the neutral particle as shown by the bottom two broken curves indicated by $V_q$ = 1 and 0.5, each corresponding to the volume of the condensate subjecting charge effect to be an entire sphere of embryo or a half sphere of embryo, respectively. The decrease in the theoretical $S_{cr}$ is attributed to a stronger interaction between water molecules and charge. This is because, as the charge locates on particle surface, more water molecules surround closer to the charge and lead to a more lowering of free energy in comparison with the case that the charge locates at the center of particle. Thermodynamically, it is reasonable and proper for a free charge to shift to any place more stable and having lower Gibbs free energy. Such a shifting in the charge location leads to a theoretical $S_{cr}$ in better agreement with the experimental $S_{cr}$. Thus, the charge shifting approximation seems to be a better model for the evaluation of the charge effect on $S_{cr}$ by the classical ion-nucleation theory.\textsuperscript{15,16,25}

Furthermore, the difference in the predicted $S_{cr}$ between the charged and neutral particles by the charge shifting approximation decreases from 0.022 (0.013) to 0.010 (0.006) as the particle size increases from 10 to 15 nm for a $V_q$ of 1 (0.5), indicating fading of the charge effect on increasing particle size. This is consistent with our experimental observation of $S_{cr}$, where the charged particles have lower $S_{cr}$ and the differences decrease from 0.075 and 0.051 to 0.031 and 0.029 as the particle size increases from 10 to 15 nm for negatively charged and positively charged particles, respectively. The fading of the charge effect is also supported by our previous observation of no obvious charge effect on nucleation for SiO$_2$ and TiO$_2$ particles with a diameter larger than 30 nm.\textsuperscript{4}

Nevertheless, quantitatively there still exists a discrepancy between the experimental $S_{cr}$ and the theoretical $S_{cr}$ predicted by the charge shifting approximation (e.g., 1.167 versus 1.199 for 10 nm negatively charged particles). Therefore, besides the possible effects due to the actual shape of the embryo and the charge location as depicted in Figs. 3(e) and 3(f), other effects, such as the effect of electrical field on surface tension, may also play an important role and have to be taken into account. The reported electric field effects on the surface tension are controversial. Various experimental methods have been used and the resultant effects are dependent on molecular dipole moment, orientation of droplet surface relative to the electric field, and the experimental techniques employed.\textsuperscript{26–28} For a droplet lying on an insulation film and subjected to an electric field between two parallel conductive plates, the liquid-vapor surface tension increases by 1%–2% for water and polar alcohol when an electric field with the magnitude of 10$^6$ V/m is applied but remains unchanged for nonpolar molecules.\textsuperscript{26,27} On the other hand, decrease in surface tension by up to 50% is observed when a water jet is subjected to an electric field created by applying a voltage of up to 8 kV perpendicular to the jet flow.\textsuperscript{26,27} Furthermore, the effect of electric field on surface tension also leads to a change in contact angle, and a decrease of contact angle with applied voltage is observed.\textsuperscript{26,27,29,30}

For our case, the electric field imposed by a charge on the embryo’s liquid-vapor and liquid-solid interfaces de-
pends on the charge location and the size of the embryo. The magnitude of the electric field can be estimated using a simple system, i.e., a charge in the center of a spherical liquid embryo. For a spherical embryo, the electric field on the surface imposed by a unit charge located at the center of the embryo can be calculated using Coulomb’s law.\(^{21}\) For water at 25 °C, the surface electric fields are calculated to be 4.59 \(\times 10^6\), 0.735 \(\times 10^6\), and 0.184 \(\times 10^6\) V/m for an embryo of radii of 2, 5, and 10 nm, respectively. For a comparison, the critical radii calculated by the nucleation theory corresponding to the experimental \(S_{cr}\) are in the range of 4.8–9 nm; this suggests that the liquid-vapor interface of the embryo could be subjected to an electric field in an order of \(10^5–10^6\) V/m. The field strength is strong enough to cause a significant reduction (up to 50%) in the liquid-vapor interface tension according to the measurements of Sato et al.,\(^{28}\) and this magnitude of decrease in surface tension contributes an additional lowering in free energy in addition to the charge effect [i.e., the last term in the right side of Eq. (1)] considered in the ion-nucleation theory, leading to a lower \(S_{cr}\) in a better agreement with experimental \(S_{cr}\). Note that based on the ion nucleation theory reductions of 20%, 11%, and 15% in the surface tension will lead to a \(S_{cr}\) lower or equal to the experimental \(S_{cr}\) for 10 nm negatively charged particles assuming the charge is (i) located at the particle center, (ii) located on the particle surface with a \(V_q\) of 1, and (iii) located on the particle surface with a \(V_q\) of 0.5, respectively. For other particles such as diameters of 12 and 15 nm, less reduction in surface tension is enough to make the calculated \(S_{cr}\) agree well with the experimental \(S_{cr}\). Therefore, if the electric field leads to a reduction in the liquid-vapor surface tension as measured by Sato et al.,\(^{28}\) the discrepancy between the experimental \(S_{cr}\) and the theoretical \(S_{cr}\) can be well explained.

Furthermore, it is interesting to note that there is an obvious sign preference, i.e., water condenses more readily on negatively charged particle, for 10 nm particles as shown in Fig. 11. The sign preference is not obvious for 15 nm particles but becomes more and more obvious as the particle size increases from 15 to 10 nm as indicated by the larger difference in \(S_{cr}\) between the negatively and the positively charged particles, where the difference increases from 0.002 to 0.014 compared to the experimental uncertainty of about 0.002–0.006. This observation, along with our previous observation\(^{4}\) of no obvious sign preference for particles larger than 30 nm in diameter, indicates that the sign preference becomes significant only when the particle is small enough. Furthermore, the observation of water condensing more readily on negatively charged particle is consistent with the sign preference observed in the condensation of water vapor on ions, where water is observed to condense at lower supersaturations on negative ions and the alcohols prefer positive ions.\(^{21}\)

So far, there is an explanation for the sign preference. Surface water molecules are believed to have the positive protons pointing toward the fluid,\(^{32}\) and the charge reversal symmetry is broken by the dipole layer. The polarization layer is also found at the liquid-vapor interface of a system of various polar molecules.\(^{16,32–36}\) If the ion reinforces this polarization, one might expect a lowered barrier for nucleation; if the ion must reorient the dipole, energy must be expended, and a higher nucleation barrier might be expected. For water, the polarization should interact unfavorably with positively charged particles and lead to the sign preference we observed. The presence of the sign preference also indicates that there is a major defect in the classical nucleation theory because it cannot differentiate between positive and negative ions.

V. SUMMARY

Condensation of a supersaturated vapor of water on nanoparticles of SiO\(_2\) was investigated in the FCC. An electrospray system is developed and has succeeded in producing SiO\(_2\) nanoparticles of less than 10 nm. The particle size distribution is controllable by the adjustment of the operation parameters such as flow rates, reactant concentration, etc. Both the peak concentration and the peak diameter increase with liquid flow rate and concentration but decrease with liquid conductivity. There exists an optimum gas flow rate to achieve a maximum peak concentration. The onset of heterogeneous nucleation was determined through measurements of removal efficiency as a function of the supersaturation along with observations of the laser light scattered by the falling droplets. Our results showed that heterogeneous nucleation is induced on neutral aerosols at critical supersaturations, agreeing well with the predictions by the Kelvin equation and slightly higher than the predictions of the Volmer theory of heterogeneous nucleation for perfectly wetted particles based on bulk physical properties. The experimental \(S_{cr}\) decreases with increasing particle size at a rate in reasonable agreement with the predictions. The effect of charge on \(S_{cr}\), measured on charged particles of 10, 12, and 15 nm, each carrying a single positive or negative charge, shows an obvious effect much higher than the theoretical predictions. The discrepancy between the experimental and theoretical charge effects on critical supersaturation can be well explained by the reduction of liquid-vapor interfacial energy due to the electric field imposed by the charge, if the electric field can lead to a reduction in surface tension as observed by Sato et al.\(^{28}\) However, the possibility that the theoretical model itself caused the discrepancy cannot be ruled out yet. Furthermore, an obvious sign preference, i.e., water condenses more readily on negatively charged particle, for 10 nm particles is observed, while the sign preference is not obvious, within the uncertainty, for 15 nm particles. The fact that the sign preference becomes more and more obvious as the particle size decreases from 15 to 10 nm indicates that the sign preference becomes significant only when the particle is small enough. The sign preference we observed agrees with the sign preference observed in the condensation of water vapor on ions.

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