The Measurement and Analysis of Microphysical Capabilities of the Condensation Nucleus of Artificial Warm Fog

DAI Meng-yan, CHEN Chun-sheng, LIU Jiang-hai, ZHANG Liang and HE Hai-yan

State Key Laboratoty of NBC Protection for Cilivian, Research Institute of Chemical Defence, Beijing, 102205 China

daidecai0558@163.com

Abstract. In this paper, the microcosmic capabilities of the condensation nucleus and fog droplets of artificial fog were observed and sampled by ELPI, SEM, XRD and LPSA. The chemical composition, number concentration, volume concentration and nucleation efficiency of the artificial condensation nucleus were gained. The condensation nucleus was mainly made up of chloride. The size distribution scope was about 0.291～1.59μm and the peak particle size was 0.609~0.942μm. The number concentration of the condensation nuclei was 3.98×10^5~4.82×10^5/cm^3, the volume concentration was 2.02×10^5~2.30×10^5μm^3/cm^3, and the maximum nucleation efficiency was 3.07×10^{12} /g. Actually, most condensation nuclei did not participate in the actual fog performing process, and the nucleation activation proportion was 13.57%. The condensation nucleus played an important role in the microphysical performance of fog droplets. However, the growing velocity of fog droplets was not identical as the catalytic performance difference of nuclei and the uneven distribution of watervapor in air. That was the reason why the fog droplets size distribution behaved the characteristic of bi-spectrum converting into uni-spectrum gradually.

1. Introduction

The cloud coagulate nucleus (CCN)in nature is the nuclei of cloud droplets and fog droplets in the environment of oversaturation, with the particle size range of about 10^{-3}～10μm. The coagulate nucleus is indispensable for the coagulation of water vapor. The meteorological change relies on the soluble nuclei such as NaCl and $(NH_4)_2SO_4$ [1-3]. The artificial cloud catalyst widely used in weather modification contains cold cloud catalyst and warm cloud catalyst, and the effective components including AgI, NaCl, $CaCl_2$ and so on [4]. The function of artificial cloud catalyst in atmosphere depends on its physicochemical characteristics [5-6], including particle size, microstructure, constituent and optical property.

We have made artificial fog based on the stimulation of formation mechanism of nature fog by fog aerosol [7]. The hygroscopic catalyst is transformed into artificial condensation nucleus with feat size distribution by the combustion of fog aerosol. Then water vapor coagulates on the condensation nucleus and the fog droplet comes into being. The condensation nucleus made up of hygroscopic inorganic salt (such as chloride) is used as warm cloud catalyst. The microphysical characteristics of condensation nucleus including constituent, number concentration and nucleation efficiency are closely related to its cloud catalytic performance [8-9]. Thus the microphysical characteristics of condensation nuclei have decisive effect on the growth process of fog droplets and would make very

different attenuation of electromagnetic waves through artificial fog [10]. In the research of cold cloud catalyst, air filled with catalyst particles is usually injected into a cloud chamber with oversaturation condition, then catalyst particles will grow into ice crystals and the nucleation efficiency could be calculated with the help of microscope [11]. Inevitably test error caused by the wind tunnel dilution system and manual operation exists in this method. More importantly, this method is inapplicable to the warm cloud catalyst research because of the entirely different mechanism of nucleation. In this work, in order to establish the inner correlation between the microphysics characteristics of condensation nucleus and fog droplet of artificial fog, they were studied by several analytical methods including the electrical low pressure impactor, scanning electron microscope, X-ray diffraction and laser particle size analyzer. The number concentration, volume concentration and nucleation efficiency of the artificial condensation nuclei and droplets were obtained. It was expected that such work would help to reveal the nucleation control and catalysis mechanism of artificial condensation nucleus, and also have important significance for the optimum of the optical extinction effect of artificial fog.

2. Experimental

2.1. Experimental instrument

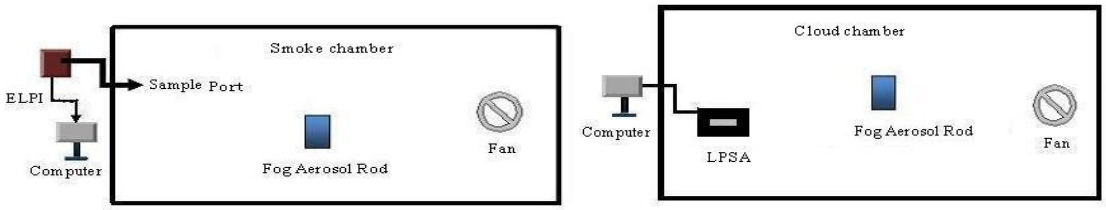
The microphysical characteristics of condensation nucleus was sampled and tested by the electrical low pressure impactor (Finland DEKATI Company). Electrical low pressure impactor (ELPI) classifies the particles into 12 size channels in the size range 0.03~10μm according to the aerodynamic diameter, such as 27.6-55nm(Channel 1), 55-93.7nm(Channel 2), 0.0937-0.155μm(Channel 3), 0.155-0.261μm(Channel 4), 0.261-0.38μm(Channel 5), 0.38-0.609μm(Channel 6), 0.609-0.942μm（Channel 7）, 0.942-1.59μm(Channel 8), 1.59-2.38μm(Channel 9), 2.38-3.97μm(Channel 10), 3.97-6.64μm(Channel 11）, 6.64-9.85μm(Channel 12). Scanning electron microscope (SEM) image of the condensation nucleus was obtained on a Hitachi S-4800 microscope (Japan). X-ray diffraction (XRD) spectrogram was tested by a Rigaku X-ray diffraction D/MAX2200 (Japan). The microphysical characteristics of fog droplets were tested by Winner311-XP Laser Particle Size Analyzer (LPSA, Jinan Winner Particle Instrument Company).

2.2. Experimental

The directions of fog aerosol contains oxidant (45~75%), bond (8~22%), combustible matter (0~10%), hygroscopic catalyzer (5~20%) and additive (1~5%) [7].

(1) Experimental method of sampling and testing of condensation nuclei

These experiments were done in a small smoke chamber with the volume of 6.375 m^3, the temperature was controlled at 14～20℃ and the relative humidity was controlled below 40%. The flow of sampling probe of the ELPI was 10L/min. Figure1(a) shows the schematic diagram of experimental set-up. 1 gram of fog aerosol was ignited by Mg rod or the high temperature gun (American Bernzomatic) respectively in each experiment. The fan stirred for 20s after combustion of fog aerosol, and the condensation nuclei were sampled and tested.



(a)Measurement of condensation nucleus (b)Measurement of fog droplets

Figure 1. Schematic diagram of experimental set-up for the measurement of condensation nuclei and fog droplets.

(2) Experimental method of testing of fog droplets

The experiments were done in a cloud chamber with the volume of 50m^3(4.4m×3.3m×3.4m), the temperature was controlled at 14~20℃ and the relative humidity was 75~80%. Figure1 (b) shows the schematic diagram of experimental set-up. 60 grams of fog aerosol was used in each experiment. The fan stirred for 20s after combustion of fog aerosol, and the fog droplets were tested.

3. Results and discussion

The condensation nuclei produced by combustion of fog aerosol would absorb water vapor and grow into fog droplets as soon as possible in suitable humidity conditions. If the microphysics performances of condensation nuclei and fog droplets are tested in the same experiment, it will be difficult for neither LPSA nor ELPI to distinguish between solid particles and fog droplets accurately. Thus the subsection measure method of condensation nuclei and fog droplets was designed to reduce the adverse effect of different dispersion space, environmental conditions and instruments.

3.1. The combustion of fog aerosol and dispersion of condensation nucleus

As shown in figure 2 the experiment results indicated that the hot air mass produced by combustion of fog aerosol was mixture of numerous condensation nuclei and manifold gas including CO_2, H_2O and O_2 calculated from the description of the fog aerosol(as shown in figure 2(a)). In the beginning, the hotair mass diffused around freely with high velocity. As a result of the difference in temperature and pressure between the hot air mass and atmospheree, the movement of hot air mass changed mostly attributed to air resistance, energy exchange and mass diffusion in the ascending process of hot air. Then the flow velocity of air mass decreased and diffused in the chamber gradually.

The relative humidity was controlled at below 40% in order to prevent the moisture absorption of condensation nucleus. In consequence, it was supposed all aerosol particles kept solid phase and there was no liquid droplets existed in the chamber. The condensation nuclei firstly suspended on the top of the chamber(as shown in figure 2(b)). It took about 5~6 minutes for the nucleus particles to sink, diffuse and evenly disperse in the chamber(as shown in figure 2(c)).

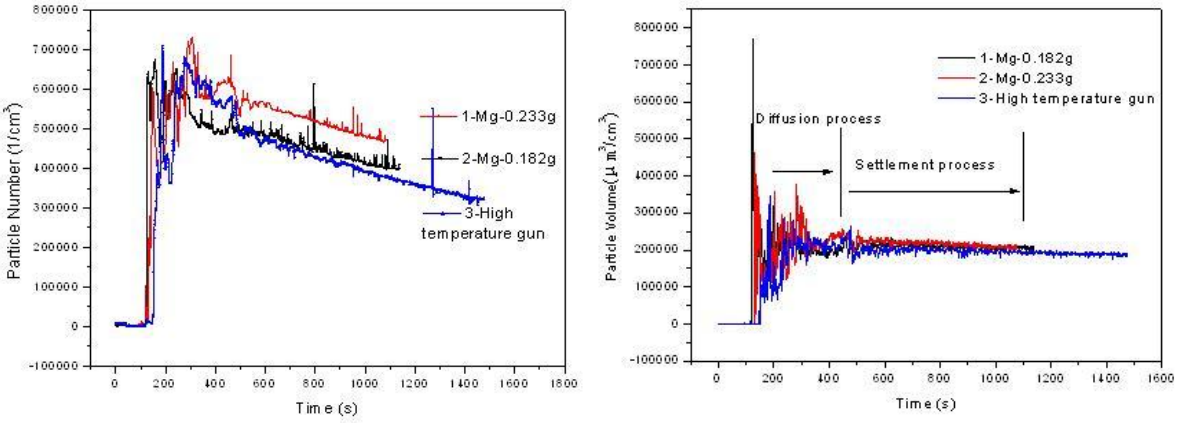
(a)Combustion process (b)10s after combustion (c)6mins after combustion

Figure 2. Photoes of combustion of fog aerosol and diffusion of condensation nucleus.

3.2. The microphysical performance of condensation nucleus

Figure3 gives the number concentration curve and volume concentration curve of condensation nuclei produced by fog aerosol ignited by Mg rod and high temperature gun respectively. The microphysics characteristics of condensation nuclei behaved similar trend of variability in the three conditions. In the time of 0~5 minutes after combustion, the number concentration and volume concentration of condensation nuclei increased rapidly(as shown in figure3(a)). In the time of 5~15 minutes the curves of number concentration and volume concentration demonstrated a tendency toward stabilization before slowly decline. Based on these results, the dispersion process of condensation nucleus particles could be divided into two steps. The first step was the freely diffusion process of particles propelled by gas expansion, and the second step was the settlement process due to gravity. The particles flowed fast

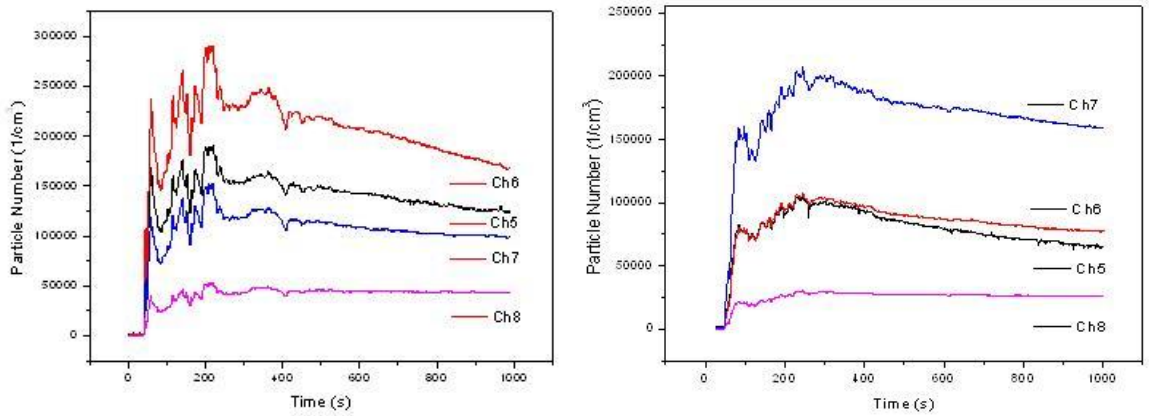
as a result of instability of diffusion process, and this leaded to the uneven distribution of condensation nuclei in the whole chamber. Accordingly, the curve of number concentration and volume concentration of the particles displayed larger fluctuation in 0~5minutes. In 5~10minutes, the freely diffusion process of particles already finished and no obvious settlement phenomena had taken place yet. Therefore, the test results of that time could be thought as the average concentration of condensation nuclei produced by fog aerosol.



(a)Number concentration curve (b)Volume concentration curve

Figure 3. Number concentration curve and volume concentration curve of condensation nuclei.

It was indicated that the number concentration of nuclei though different ignition methods varied obviously. The number concentration of nuclei ignited by Mg rod(with the mass of 0.233g) was about 20% more than that ignited by high temperature gun. A great of deal of MgO solid particles would be generated by the combustion of Mg rod, and that caused the number concentration tested much bigger. While the combustible of high temperature gun was butane, there were no solid products that would probably interfere with the measurement of condensation nuclei. It was clearly that the results obtained from the high temperature gun ignition would be more accurate.



(a)Mg ignition (b)High temperature gun ignition

Figure 4. Number concentration curves of condensation nuclei tested by ELPI.

Figure 4 gives the number concentration curves of condensation nuclei produced by fog aerosol ignited by Mg rod and high temperature gun respectively. The particle size scope of condensation

nuclei gained by different ignition methods was almost in the same size channels of ELPI. They were Channel 5(0.261-0.38μm), Channel 6(0.38-0.609μm), Channel 7(0.609-0.942μm), and Channel 8(0.942-1.59μm)). However, the peak particle size and characteristics of distribution were different. The condensation nuclei obtained by Mg ignition methods were smaller and the peak particle size was 0.38~0.609μm. The number concentration of the size channels of ELPI in a descending order was Channel 6, Channel 5, Channel 7, and Channel 8. The condensation nuclei obtained by high temperature gun ignition methods were comparatively bigger and the peak particle size was 0.609～0.942μm. The number concentration in a descending order was Channel 7, Channel 6, Channel 5, and Channel 8. Combined with figure 3 and figure 4, it was deduced that the MgO particles were mostly fine particulate matter from the fact that the main effect of MgO particles was a marked increase on the number concentration of Channel 6 and Channel 5.

Meanwhile, it was worth noting that the volume concentration curves of different ignition methods was similar as shown in figure 3(b). It was because the key factors impacting the volume concentration of aerosol particles comprised of number concentration and size distribution. According to the calculation equation of the volume concentration (V):

$$V = \int_0^\infty N_r \cdot \frac{4\pi}{3} \cdot (\frac{D_r}{2})^3 \quad (1)$$

As in equation (1), N_r was the number concentration of the particles with the diameter of D_r. The volume concentration of particles was directly proportional to the cube of diameter, so the particle size contributed much more to the volume concentration than the number concentration. Since the MgO particles were all fine particulate matter, the Mg ignition method did not affect greatly on the volume concentration of condensation nuclei.

Table 1 gives the data of the microphysical characteristics of condensation nuclei in different time. The number concentration of concentration nuclei was 3.98×10^5~4.82×10^5 /cm^3, and the volume concentration was 2.02×10^5~2.30×10^5μm^3/cm^3. The particle size distribution range was 0.261~1.59μm，and the peak particle size was 0.609~0.942μm. The number concentration of the size channels in a descending order was Channel 7, Channel 6, Channel 5, and Channel 8. The volume concentration in a descending order was Channel 7, Channel 8, Channel 6, and Channel 5. The test results just verified our analysis above that the particles of bigger size contributed much more than smaller ones on the volume concentration, and this made the distribution feature of the number concentration not consistent with that of the volume concentration. For example, the particles of channel 8 were the biggest in all. In the time of 5 minutes, the number concentration of channel 8 was only 30% of that of channel 6, but the volume concentration of channel 8 was 4 times more than that of channel 6.

Table 1. The data of the microphysical characteristics of condensation nuclei.

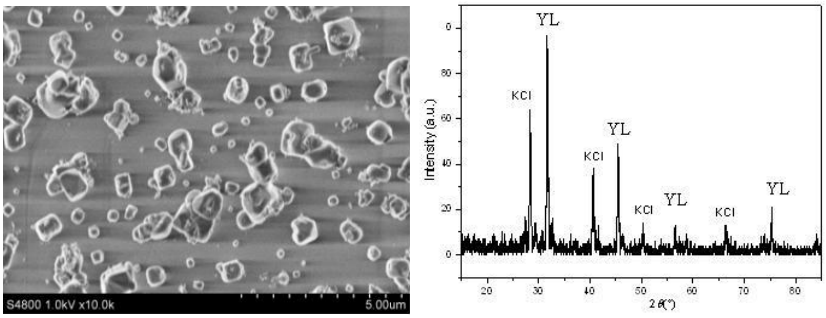
Time	ELPI Channel	Ch5	Ch6	Ch7	Ch8	Ch1-Ch12
	Size（μm）	0.261-0.38	0.38-0.609	0.609-0.942	0.942-1.59	0.03-10
5 minutes	Number concentration(/cm^3)	9.60×10^4	9.93×10^4	1.93×10^5	2.85×10^4	4.82×10^5
	Volume concentration（μm^3/cm^3）	0.15×10^4	0.59×10^4	4.35×10^4	2.72×10^4	2.30×10^5
15 minutes	Number concentration(/cm^3)	6.56×10^4	7.67×10^4	1.61×10^5	2.50×10^4	3.98×10^5
	Volume concentration（μm^3/cm^3）	0.10×10^4	0.46×10^4	3.66×10^4	2.53×10^4	2.02×10^5

3.3 The influence of condensation nuclei on the microphysical performance of fog droplets

Figure 5 gives the SEM image and XRD spectrum of condensation nuclei. The morphology of the condensation nuclei was in the shape of near-sperical orcubic and composed of chloride such as KCland YL. Defined the nucleation efficiency as the number of the condensation nuclei per gram of fog aerosol in the unit of /g:

$$\lambda_0 = \frac{c_n \times V}{m} \tag{2}$$

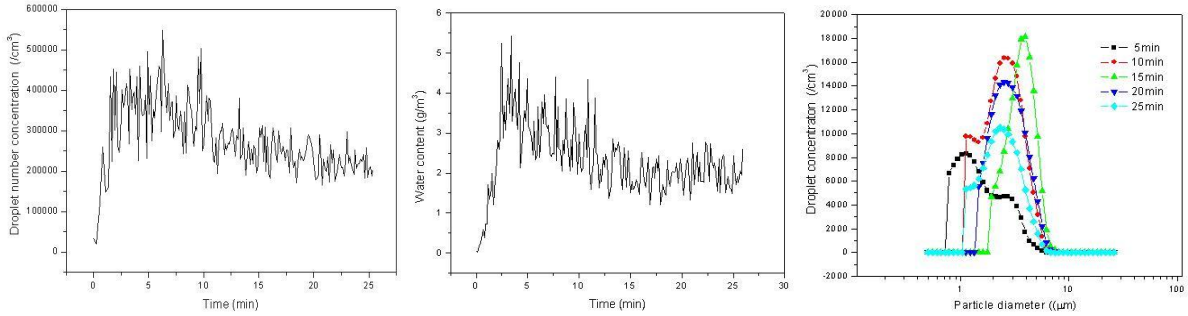
As in equation (2), C_n: the number concentration of condensation nuclei, in /cm^3; V: the volume of the chamber, in cm^3; m: the mass of fog aerosol, in gram. As the maximum number concentration was 4.82×10^5 /cm^3, the nucleation efficiency could be calculated as 3.07×10^{12}/g.



(a)SEM image(×10000) (b)XRD spectrum

Figure 5.SEM image and XRD spectrum of condensation nucleus.

Figure 6 gives the number concentration, water content and size distribution of fog droplets. The life circle of fog droplets could be divided into 4 stages: formation stage, development stage, stabilization stage and elimination stage. The formation stage was in the time of 0～3minutes, the condensation nuclei started growing into fog droplets instantly in the humidity controlled higher than the deliquescence relative humidity of chloride. The number concentration and particle size of fog droplets increased rapidly in this stage. The development stage was in 3～10 minutes, the increment speed of number concentration and particle size reduced a little than before, however, the number concentration and water content reached their maximum value in that time. The size distribution of fog droplets behaved characteristic of bimodal distribution and the peak size scope narrowed distinctly. The stabilization stage was in 10~20 minutes, the number concentration, water content and particle size became stable and decreased slightly. At the same time, the double-peak spectrum of fog droplets converted into single-peak spectrum gradually. After 20 minutes was the elimination stage, the droplets size, water content and number concentration all began to reduce. The fog would disperse little by little as the acceleration of evaporation, coalescence and settlement of fog droplets.



(a)Number concentration curve (b)Water content curve (c)Size distribution

Figure 6. Number concentration curve, water content curve and size distribution of fog droplets.

The fog droplets were grown up from condensation nuclei with moisture absorption. The microphysical characteristics of fog droplets were closely related to the catalytic performance of condensation nuclei. There was significant linear correlation between the number concentration of fog droplets and nuclei, and the size distribution and water content were important representation of the catalytic performance of condensation nuclei and the growth speed of fog droplets. Meanwhile, the watervaporplayed a crucial role on the formation of fog droplets. It was interesting to find that after the fog forming process the environmental humidity always reduced 3～5% than before. It meant that thecoagulation of condensation nuclei and formation of droplets would consume a great deal of water vapor in air and lead to decrease of humidity. Watervapor was sufficient in the formation stage and development stage of fog, and the influence of condensation nuclei on the fog droplets was also showed more obviously in these two stages. In the stabilization stage and elimination stage, the environmental humidity began to decrease and the watervapor was not enough to sustain the growth of droplets.

Although a great number of condensation nuclei were produced by fog aerosol firstly, there was fierce competition among them. Because of the uneven distribution of watervapor and the individual difference of nuclei [12], only a little part of the numerous nuclei would be able to activate in oversaturation condition and grow into fog droplets finally. Those lucky condensation nuclei were called as activated nuclei. In the formation stage of fog droplets, the number concentration of activated nuclei was impossible to measure. As the activated nuclei would transformed into fog droplets in the instant, the number concentration of fog droplets was approximately equal to the number of activated nuclei. Defined the activation proportion as the ratio of the activation nuclei to the total number of the condensation nuclei:

$$\eta = \frac{N_a}{N_0} \times 100\% \approx \frac{N_f}{N_0} \times 100\% = \frac{N_f}{\lambda_0 \times \frac{m}{V}} \times 100\% \tag{3}$$

As in equation (3), λ_0: the nucleation efficiency of fog aerosol, in /g, N_f: the number concentration of fog droplets, in /cm^3; V: the volume of the cloud chamber, in cm^3; m: the mass of fog aerosol, in gram. According to the results above, the nucleation efficiency of fog aerosol was 3.07×10^{12} /g, and the maximum number concentration of fog droplets in the formation stage was 5×10^5/cm^3. Supposed no error brought by the subsection measure method or nuclei loss, the activation proportion was calculated as follows:

$$\eta = \frac{N_f}{\lambda_0 \times \frac{m}{V}} \times 100\% = \frac{5 \times 10^5}{3.07 \times 10^{12} \times \frac{60}{50 \times 10^6}} \times 100\% = 13.57\% \tag{4}$$

It was calculated that the activation proportion was only 13.57% in ideal condition. This result suggested that most condensation nuclei did not participate in the fog forming process and the activated nuclei were real effective condensation nuclei which showed better catalytic performance.

To sum up, the condensation nuclei were of crucial importance for the microphysical characteristics of fog droplets. Owing to the microphysical performance difference of condensation nuclei and the random distribution of watervapor in the environment, the activation proportion of condensation nuclei was low and the growth rate of fog droplets was inconsistent. The size distribution of fog droplets behaved as a double-peak spectrum in the formation stage. Then the fog droplets would grow into the equilibrium size in the development stage and stabilization stage. The size distribution of fog droplets turned to a single-peak spectrum ultimately.

4. Conclusion

The microcosmic capabilities of the condensation nuclei and fog droplets of artificial fog were observed and tested by a subsection measure method. The conclusion was as follows:

(1)The microcosmic capabilities of the condensation nuclei of artificial fog were researched by ELPI, SEM, XRD and LPSA. The number concentration of concentration nuclei was 3.98×10^5~4.82×10^5 /cm^3, and the volume concentration was 2.02×10^5~2.30×10^5μm^3/cm^3. The particle size distribution range was 0.261~1.59μm, and the peak particle size was 0.609~0.942μm. The nucleation efficiency was about 3.07×10^{12} /g.

(2)Most condensation nuclei did not participated in the fog forming process because of the competition for watervapor. The activation proportion was only 13.57% in the ideal condition. The increase of activated nuclei was of more significance for the artificial fog than the improvement of nucleation efficiency.

(3)The condensation nucleus was of crucial importance for the microphysical characteristics of fog droplet. Owing to the microphysical performance difference of condensation nuclei and the random distribution of watervapor in the environment, the growth rate of fog droplets was inconsistent and the fog droplets size distribution appeared the characteristic of bimodal spectrum converting into unimodal spectrum gradually.

5. Acknowledgments

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6. References

[1] Johnson G R，Ristovski Z and Morawska L2004*J. Aerosol Sci*. **35**443-55
[2] Abderrrahim D and Abdelfetah M 2003 *Fluid Phase Equilibria*. **206**13-25
[3] Kreidenweis S M，Koehler K and DeMott P J 2005 *Atmospheric Chemistry and Physics Discussions*. **5**1357-70
[4] Rosenfeld D，Khain A and Lynn B 2007 *Atmospheric Chemistry and Physics Discussions***7**3411-24
[5] SU Zheng-jun, GUAN Li-you and SHI Ai-li 2010 *Meteorologyical Science and Technology*. **38**259-62
[6] HU Shuai，GAO Chang-tai, LIU Leiand LIU Zhi-tian 2013*Chinese Journal of Light Scaterring*.**25**338-46
[7] DAI Meng-yan, HU Bi-ru and Wu Wen-jian 2009 *Chinese Journal of Energetic Materials*. **17**708-12
[8] Kulmala M，Korhonen P and Laaksonen A 1997 *J. Aerosol Sci*.**28**749-50.
[9] Cubison M J，Ervens B and Feingold G 2008 *Atmospheric Chemistry and Physics Discussions*. **8**5629-81
[10] Kurt B and Hans G 2004 *Aerospace Science and Technology*. **8** 63–71
[11] JIN De-zhen，ZHANG Jing-hong，JINANG Zhong-han，ZHAO Ze-hui and XU Le．2012 *Climatic and Environmental Research.* **17** 666-70
[12] SHENG Pei-xuan, MAO Jie-tai and LI Jian-guo 2005*Atmospheric Physics.* Beijing: Peking University Publishing House P290-327