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Numerical study on heterogeneous behavior of fine particle growth

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Abstract

$PM_{2.5}$ is one of critical air pollutants due to its high absorbability of heavy metallic fumes, PAH and bacillary micro organisms. Such a fine particulate matter is often formed through various nucleation processes including condensation. This study attempts to find the nucleation behaviors of $PM_{2.5}$ arisen from coal power stations using a classical heterogeneous Fletcher's theory. The numerical simulation by C-language could approximate the nucleation process of $PM_{2.5}$ from water vapor, of which approach revealed the required energy for embryo formation and embryo size and nucleation rate. As a result of the calculation, it was found that wetting agents could affect the particle nucleation in vapor condensation. In particular, critical contact angle relates closely with the vapor saturation. Particle condensation could be reduced by lowering the angles. The wetting agents aid to decrease the contact angle and surface tensions, thereby may contribute to save the formation energy.

Key words : Particle nucleation, Fletcher's theory, Particle wettability, Numerical simulation

1. INTRODUCTION

Particulate matters in ambient air are a serious air pollutant. In particular, $PM_{2.5}$ refers to inhalable particle smaller than 2.5 μm in aerodynamic diameter. Hazardous matters, including heavy metals, acid oxides, organic pollutants, bacteria and virus, are enriched on $PM_{2.5}$ because of their abundant surfaces. Individuals are being harmed by $PM_{2.5}$ because they can easily pass through respiratory system to lung. The ultra fine particles with aerodynamic diameter less than 0.1 μm are more harmful since they can deposit deeper into blood, and cause diseases (Saskia and Ven, 1998; Dong *et al*., 2005; Wang *et al*., 2000; Zhu, 2002). Conventional particulate removal devices are generally less efficient in collecting $PM_{2.5}$ generated during fuel combustion. Thus, large amounts of emissions from combustion become a significant source of $PM_{2.5}$ suspended in the air. For these reasons, how to effectively remove $PM_{2.5}$ has received urgent concern in the research fields of energy and environment. Vapor heterogeneous condensation on the surfaces of the $PM_{2.5}$ is able to make the particles grow big enough to remove by conventional particulate removal devices. The process of particle enlargement by heterogeneous condensation can be divided into two steps. Firstly, the particles have to be activated, which is called nucleation or activation. Secondly, the nuclei grow to

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droplets by condensation of vapor. In the case of vapor condensation on particles, heterogeneous nucleation has determining influence on the effect of vapor condensation. Therefore, it is necessary to examine the nucleation behavior of $PM_{2.5}$ from combustion.

Efforts have been made on heterogeneous nucleation theory since Fletcher presented a theory for vapor nucleation on insoluble spherical particles with uniform surfaces for the first time (Fletcher, 1962; Fletcher, 1958). Fletcher was the first to study the heterogeneous nucleation of vapor on a solid particle with insoluble and incompletely wetted surface. Fletcher's theory is essentially an adaptation of the classical theory of nucleation on an insoluble planar surface with introduction of a curvature, in order to describe the spherical surface of the particle and the nucleating embryo. Although the kinetic coefficient whose value is somewhat uncertain is involved in the expression of nucleation rate, and it is approximate to use the microscopic contact angle to describe the interaction between nucleating substance and solid particles, Fletcher's nucleation theory is the most practical method to predict the heterogeneous nucleation behavior. According to Fletcher's theory, saturation degree of vapor has a significant influence on the nuclear behavior, thus the influence of the uncertainty of kinetic coefficient is not important. In order to avoid the nucleation kinetic coefficient, which is an uncertain value, in the calculation of nucleation rate, the adsorption theory (Hage,1984; Lee *et al*., 1998) is developed. In this theory, the condensation of vapor is regarded as an adsorption process. The critical supersaturation predicted by the adsorption theory is only slightly lower than that predicted by Fletcher's theory for most cases. The density functional theory (Padilla and Talanquer, 2001) and the molecular approach (Zapadinsky, 2005) to heterogeneous nucleation attempted to substitute the macroscopic contact angle with a microscopic fit. However, the practical applications of the two theories are limited because of the complex nature of the microscopic interaction.

So far the researches on heterogeneous nucleation of vapor on particles focus on aerosols and pure substances (Andrews, 1996; Kotzick *et al*., 1997; Chen *et al*., 1998; Chen *et al*., 1999; Chen *et al*., 2000; Chen and Tao, 2000; Sharoichenko, 2000; Lee *et al*., 2003). Direct study on supersaturated vapor nucleation on $PM_{2.5}$ from combustion is still rare. The physical and chemical properties of particles have considerable influence on heterogeneous nucleation behaviors of vapor. However, properties of fine particles from combustion are very different from aerosols. Furthermore, the particles from different sources (coal combustion, oil burning and municipal solid waste incineration) differ greatly in compositions, surface characteristics and consequent wetting abilities. Therefore, heterogeneous nucleation on fine particles from different sources needs to be studied.

Seames (2003)' research suggested that pulverized coal fly ash particles can be described as a tri-modal particle size distribution, which includes a supermicron region, a near micron region and a submicron region. Seames drew a conclusion that the vast majority of the particles in the submicron region were spheres with smooth surfaces, the near micron-sized particles appear to be in irregular shapes, and all the particles examined in submicron region appear to be primarily spherical in shape. Guo *et al*. (2005) examined the morphological of fine particles from a coal-fired power plant. The results indicate that the great majority of the fine particles are spherical, have smooth surfaces, and contain metal oxides, silicon oxides and clay minerals. Yan *et al*. (2006) investigated the morphology and composition of coal-fired $PM_{2.5}$, and the results show that the fine particles are mainly spheres with smooth, non-porous surfaces, and that they are insoluble particles of silicon-aluminum minerals. As the heterogeneous nucleation mechanism of vapor on irregular particles is extremely complex, the nucleation behavior on irregular surfaces is still unclear. Therefore, theoretical difficulties are encountered while dealing with non-spherical particles. Fortunately, a great majority of coal-fired fine particles are insoluble, smooth spherical particles. Based on this, the nucleation behaviors of vapor (with and without wetting agent) on coal-fired $PM_{2.5}$ are numerically pre-

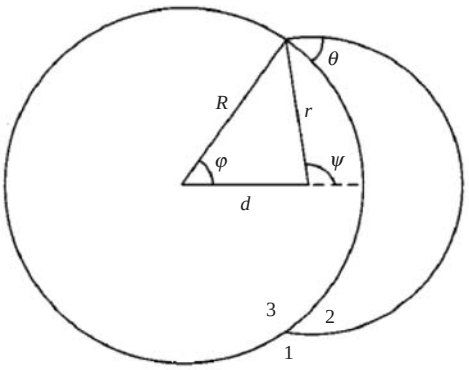

Figure 1. Schematic diagram of vapor nucleation on insoluble particle 1-vapor; 2-liquid embryo; 3-solid particle.

dicted using Fletcher's classical heterogeneous nucleation theory, and the influences of wetting agents on free energy of embryo formation, critical embryo radius, nucleation rate and critical saturation were obtained.

2. HETEROGENEOUS NUCLEATION MODEL

The embryo was assumed to be a portion of a sphere. Physical model of Fletcher's theory is schematically shown in Figure. 1. The interaction between the liquid embryo and the solid substrate can be described with the help of Young's equation

$$m=\cos\theta=(\sigma_{13}-\sigma_{23})/\sigma_{12} \tag{1}$$

where σ is the surface free energy, N · m^{-1}; the subterms 1, 2 and 3 refer to vapor, liquid and particle, respectively; θ is the contact angle between the solid particle and the liquid embryo, °; and m is the cosine of the contact angle θ.

The change of Gibbs free energy, ΔG, as a result of the embryo formation from water vapor under a constant pressure and temperature can be expressed as

$$\Delta G=\Delta G_v V_2+\sigma_{12}S_{12}+(\sigma_{23}-\sigma_{13})S_{23} \tag{2}$$

where ΔG_v, is the free energy difference per unit volume of embryo between matter in vapor phase and matter in liquid phase, J · m^{-3}; V_2 is the volume of the embryo, m^3; S_{12} and S_{23} are the areas of vapor-liquid and liquid-solid interfaces, respectively, m^2 · S_{12}, S_{23}, V_2 can be calculated by

$$S_{12}=2\pi r^2(1-\cos\psi) \tag{3}$$

$$S_{23}=2\pi R^2(1-\cos\varphi) \tag{4}$$

$$V_2=\frac{1}{3}\pi r^3(2-3\cos\psi+\cos^3\psi) -\frac{1}{3}\pi R^3(2-3\cos\varphi+\cos^3\varphi) \tag{5}$$

where r is the radius of the liquid embryo, m; R is the particle radius, m; ψ and φ are given in Figure 1.

From Figure 1, the following relationship could be derived:

$$\cos\psi=-(r-R\cos\theta)/d=-(r-Rm)/d \tag{6}$$

$$\cos\varphi=(R-r\cos\theta)/d=(R-rm)/d \tag{7}$$

$$d=(R^2+r^2-2Rrm)^{1/2} \tag{8}$$

if $(\partial G/\partial r)^*=0$, then the critical embryo radius r^* would be as follows,

$$r^*=-2\sigma_{12}/\Delta G_v \tag{9}$$

By combining eqs (9) and (2), the free energy for the critical embryo formation will be as eq. (10),

$$\Delta G^*=\frac{8\pi\sigma_{12}^3}{3(\Delta G_v)^2}f(m,x) \tag{10}$$

where

$$f(m,x)=1+\left(\frac{1-mx}{g}\right)^3+x^3\left[2-3\left(\frac{x-m}{g}\right)+\left(\frac{x-m}{g}\right)^3\right]+3mx^2\left(\frac{x-m}{g}-1\right) \tag{11}$$

$$g=(1+x^2-2mx)^{1/2} \tag{12}$$

$$x=R/r^* \tag{13}$$

If the liquid embryo is incompressible, ΔG_v can be written as (Fletcher, 1958, 1962)

$$\Delta G_v=\frac{kT}{V_L}\ln S \tag{14}$$

where, k is the Boltzmann constant, 1.38×10^{-23} J · K^{-1}; T is the vapor temperature, K; V_L is the volume of a single water molecule, 2.99×10^{-29} m^3; and S is the saturation degree of the vapor phase.

The nucleation rate, J, can be expressed as the following, according to Boltzmann distribution function of statistical physics (Lee *et al*., 1998)

$$J=4\pi R^2 K_c \exp\left(-\frac{\Delta G^*}{KT}\right) \quad (15)$$

where K_c is the kinetic coefficient of nucleation, whose value is somewhat uncertain between 10^{28} and 10^{31} m^{-2} · s^{-1}. In this paper we adopted $K_c=10^{29}$ m^{-2} · s^{-1}.

3. RESULTS AND DISCUSSION

The numerical simulation platform for vapor nucleation on an insoluble smooth particle was established using C language programming. The temperature T was set to be 298 K in this simulation. The successive approximation method was used for the computation of the critical saturation by solving the governing equations of Eqs. (10), (14), (15) in cases with given values of the surface free energy, the contact angle and the particle radius.

3.1 Influence of wettability on critical saturation

Heterogeneous nucleation depends strongly on wettablility of the particles, which is typically measured by contact angle. The critical saturation is usually taken as the saturation for which the nucleation rate is 1 s^{-1}, if calculating the nucleation rate per particle using the classical theory of heterogeneous nucleation. Critical saturation indicates ambient saturation at which a particle will promote almost immediate nucleation and condensation. The critical saturation S_{cr} of vapor nucleation on particles with a diameter in the size range 0.1 ~ 10 μm is shown in Figure 2. The curves in Figure 2 give the dependences of the critical saturation on the particle diameter with the contact angles of 20°, 10° and 5°, respectively. The critical saturation can be lowered through improving the wettability of the particles by such as decreasing the contact angle.

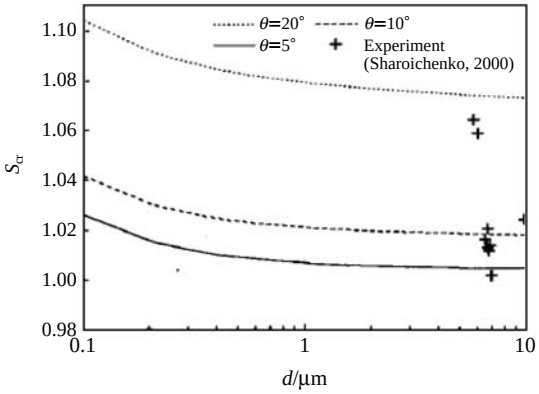

Figure 2. Critical saturation S_{cr} at different contact angles.

The discrete points in Figure 2 are taken from a reference (Sharoichenko, 2000), in which a single insoluble, smooth particle of soda lime glass is levitated by combination of thermal diffusion and electric levitation to study the nucleation behavior of the particles. From the simulation curves and the experimental data, it was found that the contact angles for the soda lime glass particles were present almost in the range of 5° ~ 20°. This is in accordance with the tested values of the contact angle for the parti-cles, which are between 7.3° to 17°.

3.2 Effect of wetting agent on nucleation behavior

Yan *et al*. (2006) tested the surface tensions of water and wetting agent solutions using the maximum bubble pressure method as well as the contact angles between water (with and without wetting agent) and $PM_{2.5}$ from coal combustion based on the Washburn penetration pressure method. The contact angle could be obtained through measurement of the pressure change in the tube when the liquid raised in the powder bed. The values of surface tensions and the contact angles are listed in Table 1. The aqueous solution concentrations were 0.50 % for all the wetting agents. From Table 1, one can see

that the wetting agents can reduce the surface tension of the liquid phase and change the contact angle between the liquid and the particle in different extents. Thus the heterogeneous nucleation ability of water vapor on the particle can be improved.

Combined with the data in Table 1, numerical simulations of the heterogeneous nucleation behaviors of water vapor (with and without wetting agent) on $PM_{2.5}$ from coal combustion were conducted.

3.2.1 Free energy of embryo formation

Heterogeneous nucleation takes place when supersaturation of the vapor phase is achieved, thereby this process can lead to form a liquid embryo. The change of Gibbs free energy of embryo formation varies with the embryo radius as shown in Figure 3, which gives the change of Gibbs free energy in the heterogeneous nucleation process in cases with and without wetting agents at the vapor saturation of 2.0 and the particle diameter of 2.5 μm. From Figure 3, it could be noted that the free energy increased at the beginning, but it decreased after passing through the maximum. The maximum change of free energy shown in Figure 3 represents the free energy of critical embryo formation ΔG^* · ΔG^* decreases rapidly while adding a wetting agent into the water. The free energy of critical embryo formation could reflect the nucleation ability of vapor if the saturation degree is kept constant. In the case of heterogeneous condensation the embryo has to pass through the free energy barrier ΔG^* in order to achieve substantial vapor condensation to form the big-sized droplet. This indicates that the $PM_{2.5}$ particles will be enlarged to relatively larger particles by vapor condensation. ΔG^* decreases rapidly while adding a wetting agent into the water, because of reducing in the contact angle and the surface tension as we can see from Table 1. The lower critical free energy is, the easier the nucleation is likely to happen. Therefore, the nucleation ability of vapor on fine particles can be improved by adding the wetting agent.

Table 1. Values of surface tension of water and aqueous wetting agent solutions and their relative contact angles with $PM_{2.5}$ from coal combustion (25°C).

Water or solution	Surface tension/ $mN \cdot m^{-1}$	Contact angle/ (°)
Water	72.90	83.02
SDBS	31.94	69.90
SDS	35.17	0
JFC	31.57	73.94
FS-310	26.09	82.14
Silanol w22	21.54	10.26

3.2.2 Critical embryo radius

The critical embryo radius corresponds to the maximum free energy of embryo formation. The free energy of embryo formation, which is not influenced by the size of the solid particle, depends mainly on the surface tension of the liquid phase and the saturation degree of vapor phase. Figure 4 gives the relationship between

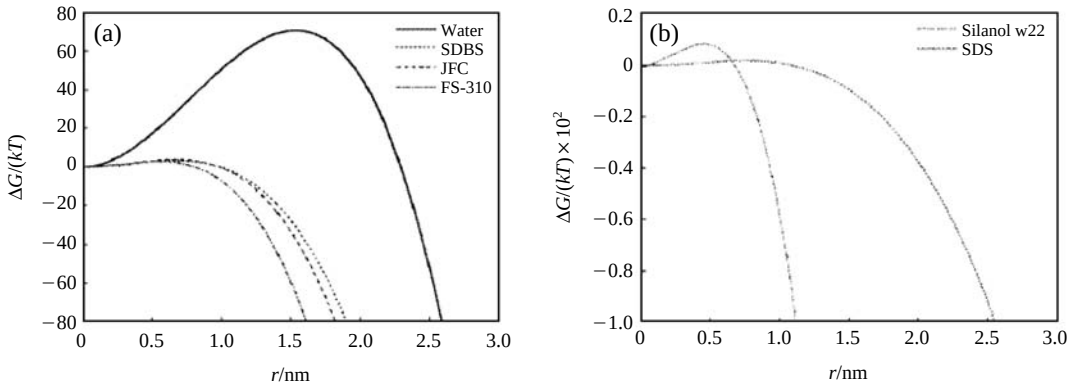

Figure 3. Dependency of relative values of nucleation free energy $\Delta G/kT$ on embryo radius r.

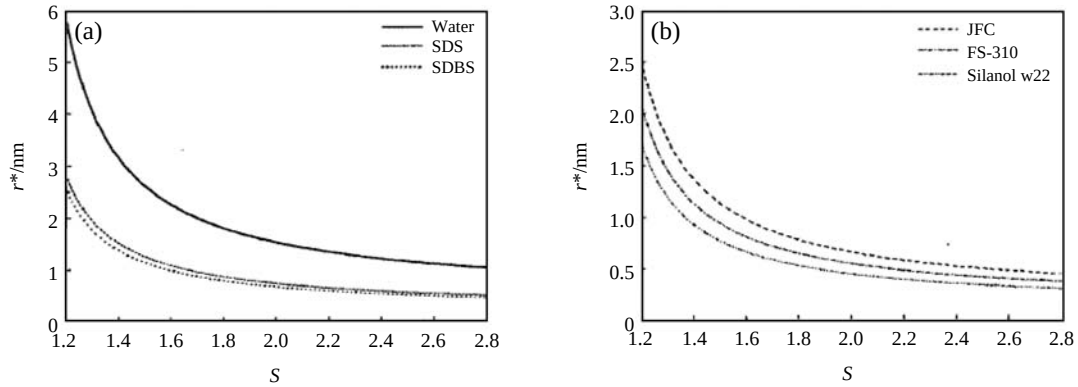

Figure 4. Dependence of critical embryo radius r^* on vapor saturation S.

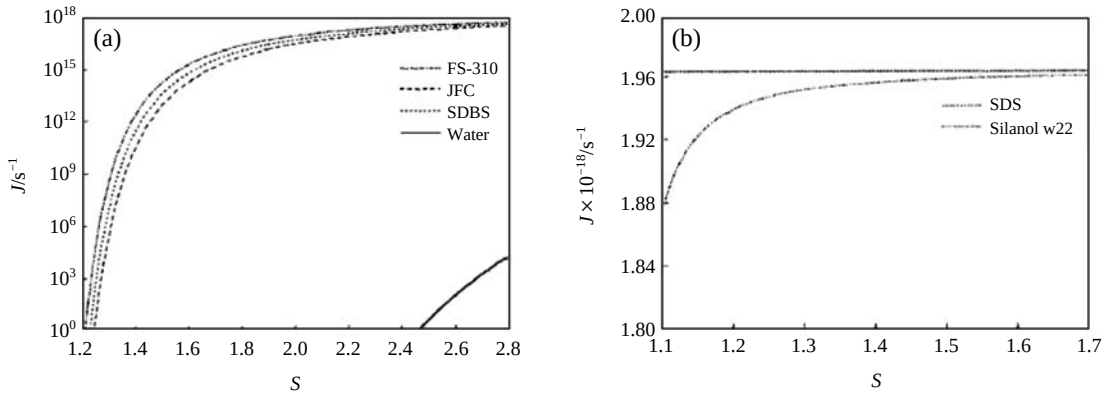

Figure 5. Dependence of nucleation rate J on vapor saturation S.

the critical embryo radius and the saturation degree of vapor under the conditions with and without wetting agent. The results indicate that the critical embryo radius decrease with the increase in saturation degree, and that the critical embryo radius decreases when the wetting agent is added at the same saturation degree. The reason is that the surface tension of the liquid phase is lowered by the wetting agent, consequently the critical embryo radius decreases.

3.2.3 Nucleation rate

The influence of saturation degree of vapor on nucleation rate at the particle diameter of 2.5 μm is given in Figure 5. As can be seen in Figure 5, the nucleation rate is below 1 s^{-1} when the saturation degree is lower than 2.4 in cases without wetting agent. However, the nucleation rate increases tens of magnitudes when the wetting agent is added. It is also can be seen that the nucleation rate J is very sensitive to the saturation degree S. The curves corresponding to the wetting agents such as FS-310, SDBS and JFC in Figure 5 are very close to each other, which is due to the cosine of the contact angle between the wetting agent solutions and the particles are almost the same. The contact angles of SDS and Silanol solutions with the particles are very small, leading to the high nucleation rate approximately 10^{18} s^{-1} at the saturation degree of 1.1.

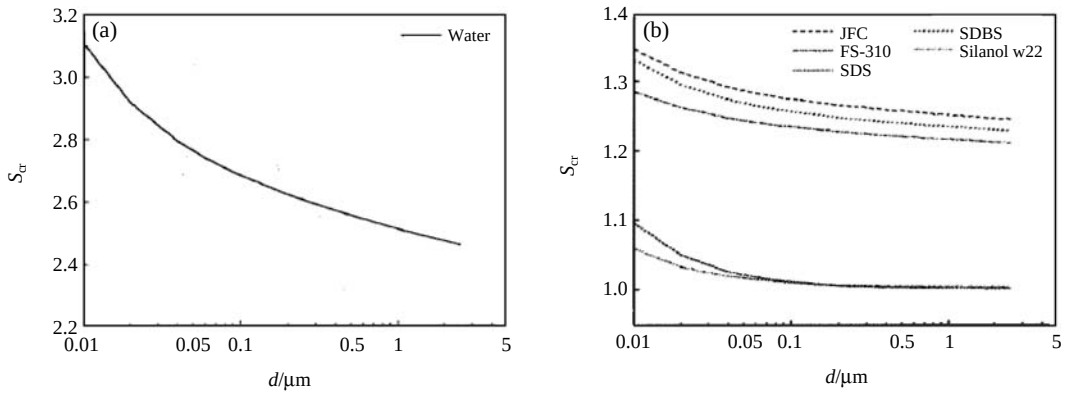

Figure 6. Dependence of critical saturation S on diameter d of $PM_{2.5}$ from coal combustion.

3.2.4 Critical saturation

Figure 6 presents the critical saturation of vapor nucleation on the fine particles in the size range 0.01～2.5 μm with and without wetting agent. The critical saturation decreased with the increase in particle diameter. The critical saturation could be lowered by means of adding wetting agent, but the effect of the wetting agents was different due to the different values of contact angles and surface tensions caused by the wetting agents. Among the five wetting agents (JFC Secondary alcohol polyoxyethylene ether), SDBS (sodium dodecyl benzene sulfonate), FS-310, Silanol w22 and SDS) used in this study, Silanol w22 and SDS (sodium dodecyl sulfate) are quite acceptable for reducing the critical saturation. For instance, when the particle diameter was 2.5 μm, the critical saturations decreased to 1.245, 1.228, 1.210, 1.003, 1.001 for the five wetting agents, respectively. With Silanol w22 and SDS, even for the ultrafine particle with a diameter of 0.01 μm, the critical saturation was below 1.1.

4. CONCLUSIONS

In order to verify the reliability of the nucleation model, the simulation results for the critical saturation due to vapor nucleation on insoluble spherical particles with smooth cover surfaces were compared with the experimental results for smooth soda lime glass spheres at the contact angles between 7.3° and 17°. The heterogeneous behavior of vapor nucleation on $PM_{2.5}$ from coal combustion in cases with and without wetting agents was numerically predicted based on the physical and chemical characteristics of the particles. The following conclusions were drawn from the theoretical and experimental work.

(1) The critical saturation depended greatly on the contact angle. Saturation degree required for vapor nucleation and condensation on fine particles could be lowered by means of reducing the contact angle.

(2) Saturation degree as high as 2.4 is necessary for water vapor to achieve heterogeneous nucleation and condensation under the ambient condition, 25°C.

(3) The wetting agents could reduce the free energy of critical embryo formation by decrease both of the surface tension and the contact angle, leading to increase of the nucleation rate and rapid decrease of the critical saturation.

(4) The wettability of the particles was found to be different from the agents. Among the five test wetting agents; JFC, SDBS, FS-310, Silanol w22 and SDS, SDS and Silanol w22 were relatively desirable, and they could facilitate the heterogeneous nucleation and condensation of $PM_{2.5}$ from coal combustion with the contact degree lower than 1.1.

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