Nanoparticle generation: The concept of a stagnation size region for condensation growth

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We demonstrate that the critical size cluster concept, commonly used in a nucleation theory, should be given some further attention. It has been implied that the supercritical cluster (size larger than critical) can grow via condensation. However, as we show, there is a size range, where the arrival of a vapor molecule onto a cluster surface leads to such a heating of the supercritical cluster that, due to possible evaporation, makes it unstable and, therefore, disables its condensation growth. The described phenomenon leads to substantial accumulation of certain size clusters in the system, which is clearly evident from our experimental investigation. The found suppression of the nucleus growth within the certain size range (exceeding critical) has fundamental implications for many systems where the generation of nanoparticles occur at high temperatures.

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The mechanism of particle formation from a vapor is a key research issue in many areas, including physics, aerosol and atmospheric sciences, chemical engineering, and others. The main concept used in order to describe nucleation is related to the critical radius, i.e., a size when a molecular cluster becomes stable. The critical diameter of the cluster d_c can be routinely derived from the expression for the change in Gibbs free energy [1] required to form a cluster of a given size. It gives [2]

$$d_c = \frac{4\sigma M}{\rho R_g T \ln S}, \tag{1}$$

where M is the molecular weight of the condensing vapor, σ is the surface tension, ρ is the mass density of the condensed cluster, T is the temperature, R_g is the gas constant, and S is the saturation ratio of the vapor. $S=P/P_e$, where P is the partial pressure of the condensing vapor and P_e is its equilibrium pressure above a flat surface at the given temperature. Expression (1) states that clusters are stable with respect to evaporation if the partial vapor pressure around the particle is greater than the equilibrium pressure above the curved surface. This equilibrium vapor pressure above the curved surface with diameter d (Kelvin effect) can be written as

$$P_d = P_e \exp\left(\frac{4\sigma M}{\rho R_g T d}\right). \tag{2}$$

The nucleation theory implies that, after reaching the critical size, clusters can grow further by condensation without any limitations. Indeed, with the condensation growth, the value of the equilibrium pressure above the growing particle (and, correspondingly, the rate of evaporation) decreases due to the increase of the particle size, while the actual vapor pressure (which determines the rate of the molecule arrival onto the particle surface) does not change. Such a consideration is valid for an isothermal system. Due to the strong dependence of P_e on the temperature (which obeys the Clausius-Clapeyron equation [1]), the function on the right-hand side of Eq. (2) is an increasing function of the temperature. Then, the latent heat of condensation released during the arrival of a single molecule onto the particle surface may lead to such a heating of the particle that the condition required for condensation growth ($P \geqslant P_d$) could be breached. The latter leads to the impossibility of the condensation growth of the cluster with the diameter exactly equal to the critical one, even though such a cluster can exist. The size of particles that can grow via condensation exceeds the critical diameter given by Eq. (1). This excess depends on the particle heating, i.e., it is determined by the value of the condensation heat and the efficiency of the heat transfer from the particle to the surrounding. If a high efficiency of the heat exchange between the particle and surrounding is assumed, then the cluster heating is not significant. At the same time, there are systems where both the low efficiency of heat transfer between the particle and the surrounding and the high condensation heat release occur. This is the case, for example, during metal combustion when the cluster heating would be significant. Note that the nanooxides generated during metal combustion (unlike those obtained by other methods) possess unique properties [3,4], which determines the interest in studying their formation [5–7]. Here we demonstrate the suppression of the nucleus growth within the certain size range (exceeding critical) during nanoparticle formation by metal combustion. The found phenomenon has fundamental implications for many systems where the generation of nanoparticles occur at high temperatures.

The small value of the energy accommodation coefficient at high temperatures [8,9] makes the conduction heat transfer between the nanoparticles and the surrounding inefficient. Then, the particle overheating ΔT due to the arrival of a single molecule onto the particle with a diameter d can reach a maximum possible value of

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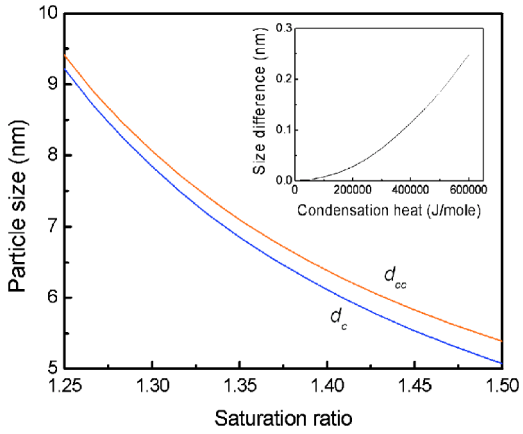

FIG. 1. (Color online) The minimal diameter of the molecular cluster d_{cc}, which can grow via condensation and the critical diameter d_c [Eq. (1)] vs the saturation ratio calculated for MgO at the following parameters: $M=0.04$ kg mol^{-1}, $\sigma=1$ J m^{-2}, $\rho=3600$ kg m^{-3}, $E=600$ kJ mol^{-1}, $c_p=60$ J mol^{-1} K^{-1}, and $T=2600$ K. The inset shows the calculated difference between d_{cc} and d_c vs E at the saturation ratio $S=1.35$.

$$\Delta T = \frac{6E}{\pi c_p \rho (d+\Delta d)^3 N_A}, \tag{3}$$

where the increase of the particle radius

$$\Delta d = \left[\left(1+\frac{6M}{\pi\rho d^3 N_A}\right)^{1/3} - 1\right] d, \tag{4}$$

with E representing the condensation heat, c_p is the heat capacity of the condensed particle, and N_A is the Avogadro constant.

If the pressure P_d calculated by Eq. (2) at a final particle temperature $T+\Delta T$ and a final diameter $d+\Delta d$ is greater than the actual vapor pressure P, then the overheated particle of an initial radius d is unstable with respect to evaporation. This means that the condensation on the corresponding particle cannot occur.

Using Eqs. (2)–(4) we can obtain the diameter of the particle d_{cc}, which, after condensation of the single molecule, becomes of the critical size (at the temperature $T+\Delta T$ and the diameter $d+\Delta d$) with respect to the actual partial vapor pressure. Following the above, the diameter d_{cc} is a minimal size of the molecular cluster, which can grow via condensation. It is obvious that $d_{cc}>d_c$. Figure 1 shows the calculated dependence of d_{cc} and d_c on the saturation ratio. Calculations were performed for MgO ($M=0.04$ kg mol^{-1}, $\sigma=1$ J m^{-2}, $\rho=3600$ kg m^{-3}, $E=600$ kJ mol^{-1}, and $c_p=60$ J mol^{-1} K^{-1}) at the typical temperature $T=2600$ K realized in the particle generation zone during Mg combustion [5,10]. The choice of MgO for calculations is related to the experiment discussed later.

As one can see, in order to grow via condensation, the particle should have the diameter $d\geqslant d_{cc}=7.1$ nm at the saturation ratio $S=1.35$, while at this saturation ratio the particle can exist if it has the diameter $d\geqslant d_c=6.85$ nm. The number of molecules in the 7.1 nm cluster is about 1.01×10^4, while in the 6.85 nm cluster it is about 9.09×10^4. Then, the difference between these clusters, which consists of about 1000 molecules, looks significant.

The decrease of the saturation ratio [represented by the logarithm in Eq. (1)] necessarily leads to the increase of d_{cc}. The latter reduces the overheating effect from condensation of the single molecule, and, consequently, the shrinkage of the difference between d_{cc} and d_c with decrease of S is becoming easily understood.

In order to demonstrate the role of the heat of condensation in the discussed phenomenon, the inset in Fig. 1 shows the difference between d_{cc} and d_c versus the heat of condensation E. As one can understand, at the small E the difference between d_{cc} and d_c is negligible.

The considered case corresponds to the maximum possible value of the particle overheating caused by the heat generated as the result of condensation of each single molecule arrived on the particle surface. In the case, when the energy accommodation coefficient describing the efficiency of the heat transfer to the surrounding is not vanishing, some portion of the condensation heat is conducted away reducing the estimated effect. The dissipated condensation heat can be estimated by considering the flux of the condensing molecules together with the flux of surrounding gases arriving on the particle surface. Some rough evaluation shows that the value

$$\eta = \frac{R_g \Delta T}{E}\frac{P_g}{P} \tag{5}$$

controls the fraction of condensation heat conducted away. Here ΔT is the value calculated by Eq. (3) and P_g is the total gas pressure. If $\eta\gg1$, then this fraction tends to unity hindering the considered effect. If $\eta\ll1$, then this fraction is negligible and the considered effect may take place even at the energy accommodation coefficient close to unity. Note that the detail consideration of the role of the conductive heat transfer in dissipation of the condensation heat is beyond the scope of the present Brief Report.

The impossibility of the cluster to grow if its size is smaller than d_{cc} (i.e., stagnation of the condensation growth) would lead to accumulation of clusters with size between d_{cc} and d_c in the system-generating nanoparticles. This peculiarity of the particle size distribution may be distinguished in the experiment.

We studied the nanoparticle generation during a Mg particle combustion in order to observe the described phenomenon. As known, MgO nanoparticles are formed from the gaseous MgO in a narrow spherical layer twice the initial Mg particle size [11]. Because of natural convection, the growing nanoparticles travel upward.

In the experiment, a 3 mm Mg particle supported by a 250 μm tungsten wire was ignited by a small propane-air diffusion flame, which was removed immediately after the commencement of the particle combustion. The typical burning time under these conditions was on the order of 10 s. A tweezers-type support holding the transmission electron microscope (TEM) grids was attached to the vertical rod. The quick rod rotation around the vertical axis allowed the very short grid residence within the MgO generation zone. Taking

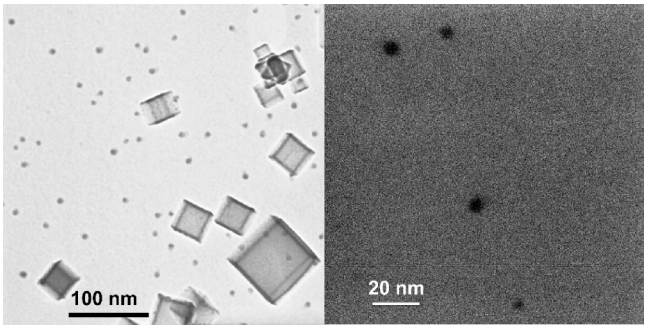

FIG. 2. The typical TEM images of the probe collected from the nanoparticle generation zone during a Mg particle combustion taken at different magnifications.

the radius of the TEM grid trajectory about 200 mm and its path within the generation zone about 5 mm, we estimated the grid residence time within the generation zone to be about 1 ms at the rotation rate about three periods per second we used. It is this small grid residence time within the generation zone that allows one to consider the probe as a snapshot. The typical TEM image of the collected probe is shown in Fig. 2. Small shapeless particles are clearly seen together with the mature MgO nanoparticles of cubic shape. Figure 3 shows size distribution of the shapeless and cubic particles. Note that the shapeless particle size distribution is normalized with respect to the number of particles smaller than 15 nm, while the cube size distribution is normalized with respect to the number of particles exceeding 15 nm. It is worth noting that the analysis of variation of the cube size distributions with the height derived from the probes collected at different heights allowed us to confirm some peculiarities of the surface growth of MgO nanoparticles [7].

The shapeless clusters can be undoubtedly considered as nuclei to form the mature MgO cubes. These cubes have grown below the collecting height. The clear size gap between the nuclei and the cubic nanoparticles (see Fig. 3) corresponds to a nucleus accumulation in the system. The peak on the size distribution of the shapeless clusters seen at about 7 nm confirms that the nucleus accumulation occurs around this size. The above-described phenomenon of the cluster impossibility to grow if its size is smaller than d_{cc} is the origin of this accumulation.

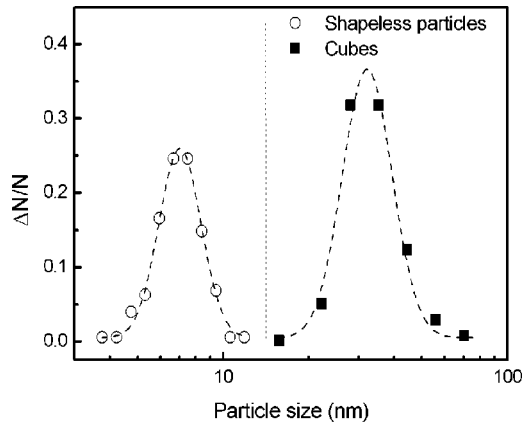

FIG. 3. Size distributions of particles collected from the generation zone during a Mg particle combustion. The shapeless particle size distribution is normalized with respect to the number of particles smaller than 15 nm, while the cube size distribution is normalized with respect to the number of particles exceeding 15 nm. Dashed lines are guides for eye.

The found stagnation of the nucleus growth within the certain size range followed by the accumulation of particles of this size can have implications for many systems where the generation of nanoparticles occur at high temperatures.

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