



Droplet evaporation on a substrate at the final stage of Low Pressure Spray Pyrolysis and the final morphology of nanoparticles



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ABSTRACT

For lowered pressure conditions femtoliter droplets evaporation on metallic substrate is investigated by experimental and theoretical methods. Simulation results of the kinetics of droplet evaporation, which substantially used the pinning effect, are presented. It was shown that the evaporation time of a droplet with the height 5 μm is about 0.01 s. For evaporation on the substrate droplets of aqueous solution with nanoparticles inside it was predicted the formation of the core–shell structure of nanoparticles. Qualitative confirmation of this effect is obtained. For Low-Pressure Spray Pyrolysis of droplets of aqueous solution of salts, the core is a metal oxide and the shell is a deposited layer of the initial salt.

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1. Introduction

A substantial drawback of the vast majority methods of nanoparticles production is their low efficiency and high energy consumption. But methods based on the use spray pyrolysis seem to be significantly better [1–3]. One of the most effective methods is so called Low Pressure Spray Pyrolysis (LPSP) [4–8], because solid nanoparticles are formed inside a liquid solution. Therefore the free energy for developing of the nanoparticles surfaces has a relatively low value. This is quite understandable because the surface tension between the solid and liquid phases is substantially lower than in gas phase–solid phase.

From engineering point of view the LPSP occurs after micron size droplets of aqueous solution are delivered into an aerosol reactor at low pressure (20–80 Torr). After fast evaporation in the aerosol reactor, the droplets are deposited on a warm metallic substrate by means of electrostatic field. Finally all droplets on the substrate are dried. The deposited dried material is actually an agglomeration of nanoparticles.

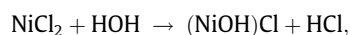
Nanoparticles of different substances have already been obtained by LPSP, such as, titan oxides [6], nickel oxides, and rare earth metal oxides [7], even carbon nanofibers [8]. Nonetheless there are questions why a micron size droplet works as a chemical microreactor, what heat and mass transfer processes cause thermodynamic and chemical instability of aqueous solution? It is worthy to note that formation of supersaturated solution is the prerequisite for nanoparticle formation from the mother phase [9].

It was already shown that in a low-pressure aerosol reactor the fast evaporative cooling of droplets takes place. In particularly, the cooling rate can amount to 200,000 K/s [10], thus a supersaturated solution is formed inside a femtoliter droplet [11]. Usually, homogeneous nucleation starts in this supersaturated solution. If colloid precursors have been inserted into the solution before dispersion, a dissolved salt usually precipitates on colloid precursors.

The final morphology of an ensemble of formed nanoparticles depends strongly on lifetime of the droplet in aerosol reactor. The droplet lifetime determines how significant is the contribution of coalescence to a variation of the morphology of nanoparticles ensemble. It was also shown that for a relatively short lifetime the final morphology is determined by two independent physical processes: droplet evaporation and Brownian diffusion of nanoparticles [12,13]. The formation of nanoparticles during LPSP is sketched in Fig. 1 [13].

It is important to mention that due to the powerful low-pressure evaporative cooling droplets temperature increase only by several tens of degrees in the high-temperature aerosol reactor used in LPSP [14]. Therefore we are conducted our experiments only at room temperature.

To the best of our knowledge the chemical kinetics of LPSP has not as yet been developed. Undoubtedly, the first step is the equilibrium dissociation of salts on ions in water. The most important step is nucleation of dissolved salt and formation of nanometer solid clusters in an aqueous solution. It is now generally agreed that the energy barrier of some elementary chemical reaction can be drastically reduced on the cluster surface [15]. For example for a cluster of nickel chloride in water we suppose that the following chemical reactions take place:



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Nomenclature

| | |
|-------|--|
| c_l | specific heat of water (J/(kg K)) |
| c | heat capacity per molecule in gas phase (J/K) |
| D | diffusion coefficient (m ² /s) |
| F | energy flow (W/m ²) |
| h | height of a droplet (m) |
| k | Boltzmann constant (J/K) |
| m | mass of a molecule (kg) |
| n | the number density of dissolve molecules of salt |
| p | pressure (Pa) |
| R | radius (m) |
| S | supersaturation of solution in a droplet |
| T | temperature (K) |
| t | time (s) |
| U | heat per molecule (J) |
| v | velocity (m/s) |

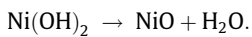
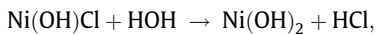
Greeks

| | |
|-----------|--|
| Δ | shell thickness, m |
| λ | heat conductivity coefficient (W/m ² K) |

| | |
|----------|-------------------------------------|
| ρ | density (kg/m ³) |
| σ | surface tension (J/m ²) |

Subscripts

| | |
|------|-----------------------|
| c | core |
| d | droplet |
| eq | equilibrium |
| g | carrier gas |
| l | liquid (water) |
| n | nanoparticle |
| s | saturated water vapor |
| sb | substrate |
| sf | droplet surface |



Furthermore, some specific physical factors enhance this route of chemical transformations. At first, molecules of HCl evaporate from the droplet surface in low-pressure environment. The synthesis of nickel oxide nanoparticles from micron-size droplets of nickel chloride aqueous solution in low-pressure aerosol reactor was described in [7]. Low-temperature synthesis of nanoparticles of nickel oxide has already been reported in our publications [16,17].

This paper is devoted to the last stage of LPSP, namely, the free molecular regime of the evaporation of the femtoliter droplet with nanoparticles on a heated substrate. Additionally we study the formation of the core-shell morphology of nanoparticles due to deposition of the salt. The paper is organized as followings. First we consider mathematical model of the evaporation of a droplet with nanoparticles on a substrate. Then we present the simulation results. In the third section we compare the simulation results with experimental data. Finally, we discuss the obtained results and prospects for future physical researches concerned with the LPSP.

2. Mathematical model of formation of the core-shell structure during evaporation

It is now widely recognized that the pinning effect is observed during evaporation of relatively small droplets on a substrate. The physical meaning of this effect is that the droplet diameter is practically constant during evaporation and only the droplet height decreases significantly [18–22]. The reason of this effect is that there are huge temperature gradients on the droplet edge near

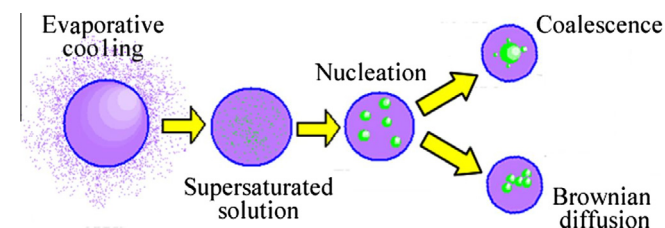


Fig. 1. Sketch of formation of nanoparticles during LPSP.

the substrate. For mathematical model due to the pinning effect we approximately replace a convex shape of a droplet by the cylindrical one (see Fig. 2) [20].

We consider the low-pressure evaporation of droplet on a warm metallic substrate, so we can assume that as the substrate heat conductivity is high enough therefore the substrate temperature under the droplet has to be constant during evaporation. Also, we assume that the total volume of nanoparticles inside the droplet is significantly less than the droplet volume. Besides it is easy to show that inside the micron-size droplet there are no steady-state convective flows. The characteristic time of hydrodynamic decay τ of a velocity field is about 10^{-6} s for water droplet with height $h \sim 2 \mu\text{m}$. Value of τ is characterized by the expression

$$\tau \sim \rho h^2 / \mu,$$

where ρ and μ are the specific mass density and the viscosity of the solution. Hence, in quasi-steady state approximation we have the linear profile of temperature inside the droplet. In the free molecular approximation the change in the droplet height is described by the following equation:

$$\frac{dh}{dt} = v = \frac{m}{\rho_l} \left(\frac{p}{\sqrt{2\pi m k T_g}} - \frac{p_s(T_{sf})}{\sqrt{2\pi m k T_{sf}}} \right), \quad (1)$$

where h is the droplet height, m is the mass of molecule of volatile component (in the simplest case, water), p is the partial pressure of water in gas phase, p_s is saturated vapor pressure, T_g и T_{sf} are temperature of the gas mixture and the temperature of evaporative surface of the droplet, respectively, and k is the Boltzmann's constant.

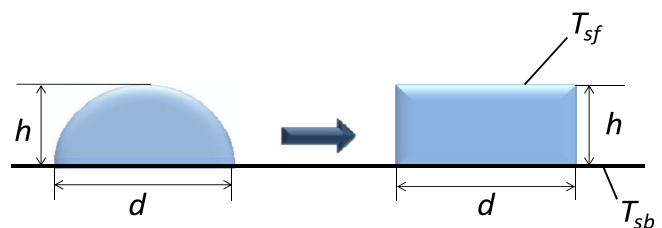


Fig. 2. Transition to a one-dimensional mathematical model of droplet evaporation on a substrate.

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