The Formation of Ultrafine Particles of Metal Sulfide by the Electrostatic Spray Pyrolysis Method[†]

Kikuo Okuyama, I. Wuled Lenggoro
and Norikazu Tagami

Department of Chemical Engineering,
Hiroshima University*

Shinkichi Tamaki

Department of Industrial Engineering,
Kinki University**

Noboru Tohge

Department of Metallurgical Engineering,
Kinki University**

Abstract

In the preparation of fine particles of metal sulfide such as zinc sulfide and cadmium sulfide using the spray pyrolysis method, the electrostatic spray method was applied to atomize the starting solutions. The optimum operation conditions where the droplets could be generated from a Taylor cone were examined experimentally. It was shown that the use of the electrostatic spray pyrolysis method is available for preparing the several dozens nanometer-sized fine particles, in comparison with a typical ultrasonic spray pyrolysis method that produced the several hundreds nanometer size.

1. Introduction

Functional fine particles were used as raw materials of ceramics, pigment, electronics, magnetic, fluorescence materials. It is important to control their size, distributions, composition/chemistry, and morphology of the prepared fine particles. Among the production methods of particles, spray pyrolysis has been widely used to prepare continuously spherical, high purity, chemistry-controlled products at relatively high production rate. Using this method, the authors have recently prepared several metal oxide and composites particles¹⁻⁵⁾.

Generally, in spray pyrolysis technique, aqueous solutions of metal salts were used as starting solutions to be sprayed to droplets by mechanical atomizations. The droplets thus generated would be introduced to heated furnace and then pyrolyzed to product the solid particles as the final products. Usually, some typical atomizers such as the ultrasonic or the twin-fluid flow nozzles used in spray

pyrolysis method can generate droplets with 4-5 μm in average, as the lower limits. As the results, the prepared particles have their average sizes in sub-micron order, 0.1 to 1.0 μm , and it is difficult to prepare the ultrafine particles below 0.1 μm . By keeping the composition and the spherical shape of the prepared particles, there are two ways to reduce the particle sizes. First, by decreasing the concentration of the starting solutions and another way is by using an atomizer method that can generate finer droplets down to submicron order. The electrostatic sprays have been reported as the method that can generate finer droplets. By controlling the properties of the liquids, the droplet diameter could be attained down to 1 micron or submicron. The applications of electrospray method as an atomizer in spray pyrolysis process to produce some functional particles such as SnO_2 or Y_2O_3 have been reported^{6,7)}.

In this study, the availability of the electrospray pyrolysis, on the preparation of fine particles of zinc sulfide, ZnS and cadmium sulfide, CdS are firstly presented. First, the relation of the experimental parameters and the optimum production rate, i.e., the number concentration of generated droplets of the device is investigated. The composition, size,

* 1-4-1, Kagamiyama, Higashi-Hiroshima 739 Japan.

**3-4-1 Kowakae, Higashi-Osaka 577 Japan.

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and morphology of prepared metal sulfide particles are compared to those prepared by an ultrasonic spray pyrolysis, previously^{9,10}. Both CdS and ZnS, the materials prepared in this study are mainly used as fluorescence materials, which are able to emit the fluorescence by the excitations of some sources such as electrons or X-rays. For example, by doping ZnS fine particle with Ag, the blue color emitting can be generated and the image display in Braun tube is one of its application. In fact, in the practical use of that fluorescence materials, several microns or somewhat larger particles were used, so it is interested in preparing finer metal sulfide particles.

2. The principle of electrospray

Electrospray phenomenon has been described in the beginning of this century, and there were considerable studies and reports on it, including their various applications such as spraying methods for liquid painting, ink-jet printer, and mostly in mass spectrometry areas. The principle of the droplet formation using the electrospray technique is shown in **Figure 1**. **Figure 1(a)** shows a metal nozzle serving both as a liquid supplier and an electrode where D.C. high voltage was applied, and a metal plate used as a grounded electrode. At the nozzle tip, a liquid meniscus was charged by electrostatic forces, and with a balance of surface tension or gravity, the meniscus is formed to a liquid cone. The expression "Taylor cone" is often used for the cone, since Taylor¹¹ has reported for the first time an analytical study on the formation of liquid cone. When the electrostatic force exceeds the liquid surface tension, the cone apex will be exerted to a liquid jet, and due to its instability, the droplets are generated by the breakup of the jet.

In this study, at first the experimental conditions such as applied voltages, liquid flow rates and solution concentrations where the stable Taylor cones can form, are investigated. Then the preparation of fine metal sulfide particles by using the device, is presented.

3. Experimental system and procedure

As starting solutions, ethanol was chosen as a solvent to dissolve the solutes containing the low cost cadmium nitrate $\text{Cd}(\text{NO}_3)_2$, or zinc nitrate $\text{Zn}(\text{NO}_3)_2$, with thiourea $(\text{NH}_2)_2\text{SC}$, as the sources of Cd, Zn and S, respectively in room temperature. In the solutions, thiourea complexes are formed, and

Fig. 1 Schematic of the droplet formation by electrospray atomization

the droplets containing these complexes can be thermally decomposed to form CdS or ZnS particles.

The use of solutions containing thiourea complexes also have been already reported to prepare metal sulfide films by the dip-coating and other processes^{12–15}. In this study, the molar ratio of cadmium nitrate or zinc nitrate to thiourea was kept at 1:2, respectively¹⁶.

The electrospray pyrolysis system used for the preparation of ZnS and CdS fine particles is schematically shown in **Figure 2**. The system is consisted of i) an atomizer, which generates the droplets from the solutions, ii) a reaction furnace, where the solution droplets decompose to form fine particles, and iii) a diffusion charging-type electrostatic

Fig. 2 The experimental system of the electrostatic spray pyrolysis, with details of the 4 nozzles position

precipitator.

The electrospray system was consisted of brass nozzles which have outer and inner diameter of 10 and 1 mm and a porous disk type brass plate used as a grounded electrode. Their distance was kept constant at 15 mm. In a complete set, four nozzles were set to configure a square with each side length is 45 mm. The tubular furnace used in the present study was a quartz glass tube of 15 mm-inner diameter and about 100 mm-length. The starting solution was supplied, by syringe pump (Harvard Apparatus, Model 55) that allows a constant liquid flow rate, to metal nozzles where the potential difference is applied between that and the metal plate. The generated droplets were carried to the reaction furnace by an inactive N_2 gas, at the flow rate of 2.0 l/min. After passing some phenomena occurred inside the droplet, such as the evaporation of ethanol and thermal decomposition, the solid metal sulfide particles are formed. The particles generated from the furnace outlet are collected using an electrostatic precipitator. The composition, size and morphology of particles are examined by X-ray diffraction, transmission and scanning electron microscopy (TEM and SEM), respectively. A Condensation Nucleus Counter, CNC (TSI, model 3020) was also placed at the furnace outlet to count the number concentration of generated droplets or particles in aerosol state.

4. Result and discussion

4.1 Effects of operating conditions on droplet generation

First, the influences of the experimental parameters on the number concentration of generated droplets or particles were investigated, mainly by spraying ZnS-preparation solution (zinc nitrate, thiourea and ethanol) by using one to four nozzles. Figure 3 shows that the particle number concentrations increase with increasing applied voltages at one and four nozzles. The liquid flow rate supplied to each nozzle was 10 ml/h and the solution concentration was fixed to be 0.05 mol/l. The experimental values were averaged since there were some fluctuations in the counting of the CNC. Especially in the range between 6 and 7 kV, the particle number concentrations increase drastically because the liquid meniscus began to form a Taylor cone at near 7 kV. The Taylor cone cannot be formed in the voltage less than 6 kV. The number concentration increases gradually at the applied voltage greater than 7 kV. At the voltage greater than 9 kV, some spark discharges are frequently observed and the particle number concentration increases to the value out of the measurable range of the CNC ($>10^7$ particles/cm³).

Figure 4 shows the changes in particle number concentrations when the supplied solution flow rate was varied at a constant applied voltage (8 kV) and at single or four nozzles cases. Both cases show a slight increase in particle number concentration as flow rate was increased. In single nozzle case, when

Fig. 3 Influence of voltage on droplet number concentration. (Solution concentration is 0.05 mol/l, flow rate is 10 ml/h)

flow rate was changed from 5 to 10 ml/h, the number concentration increases about two times, but not as the change from 10 to 20 ml/h where the number concentration is only increased slightly. This is due to the requirement of the liquid at the amount of flow rate to form a stable Taylor cone at an arbitrary applied voltage. In the experimental conditions of **Figure 4**, the stable Taylor cones were formed at flow rate less than 10 ml/hr, and at higher value, of 20 ml/h, the unstable cones were formed and that cone apex or the jet was skewed towards impermanent directions. This behavior enhanced the deposition of the droplets onto the chamber walls, and as a result it made a slight increase in particle number concentrations and decreased the throughput efficiency of the spray chamber. In the other words, it is necessary to use the other electrode configurations to form a stable Taylor cone at higher liquid flow rates.

The change of the particle number concentrations is shown in **Figure 5** when the solute concentrations of spray liquid were varied at four nozzles case. Generally, the particle number concentration increases with increasing solution concentrations, but it is almost constant above 0.01 mol/l. The droplet number concentrations of ethanol or 0.005 mol/l solution are two order smaller compared to the highest value. It was easier to form and control the stable liquid cones at lower solution concentration. At higher solution concentrations, the formation of unstable liquid cones were frequently observed. A further investigation is necessary, since the concentration changes of the solutions also will change the liquid physical properties, such as electrical conductivity, permittivity, viscosity and surface tension, which have been considered as the main parameters in the electrosprays¹⁷⁾.

Table 1 shows the influence of the number of nozzles on particle number concentrations, at applied voltage of 8 kV and liquids flow rate of 10 ml/h were supplied to each nozzle. Changes of 1 to 2 or 2 to 4 nozzles increased the number concentrations about twice, but there are only a slight

Table 1 Influence of the number of nozzles on droplet number concentration. (Solution flow rate is 10 ml/h, solution concentration is 0.05 mol/l, voltage is 8 kV)

Number of nozzles	Droplet number concentrations [$\#/\text{cm}^3$]
1	6.20×10^5
2	1.20×10^6
3	2.25×10^6
4	2.50×10^6

Fig. 4 Influence of solution flow rate on droplet number concentration. (Voltage is 8 kV, solution concentration is 0.05 mol/l)

Fig. 5 Influence of solution concentration on droplet number concentration. (Flow rate is 10 ml/h, voltage is 8 kV, 4 nozzles)

increase from 2 to 3 nozzles, not a linear relation. The asymmetrical configuration of 3 nozzles makes a different electrical field than the others, and this may be influence the stability of the Taylor cones.

It should be noted that in this study the droplets size was not measured directly, but only the changes of the droplet number concentrations are investigated. The droplet sizes are predicted from the SEM or TEM photographs of prepared particles and by using the calculation described later.

After considering some experimental conditions, the fine particles of CdS and ZnS were prepared and sampled. The experimental condition which could

generate the highest droplet number concentration, i.e., the highest production rate, was used as a basis condition and it was four nozzles, 8 kV applied voltage, 10 ml/h liquid flow rate per nozzle.

4.2 Experimental results

The concentrations of CdS-preparation solutions were changed 3 runs; 0.001, 0.005, 0.01 mol/l, and those of ZnS were 6 runs; 0.005, 0.01, 0.03, 0.05, 0.07, 0.1 mol/l, respectively. Their characteristics were investigated with the furnace temperatures at 500°C and N₂ carrier gas of 2.0 l/min.

Figure 6 shows X-ray diffraction patterns of CdS particles. This result verifies the availability of the electro-spray pyrolysis as a method to prepare the fine metal sulfide particles. Comparing to the particles prepared by an ultrasonic spray pyrolysis,

electrospray pyrolysed particles have broader diffraction peaks. One reason might be that the decreasing crystalline size of those ultrafine particles, as mentioned later, makes the diffraction waves interference weaken, not due to the poor crystallization during the process.

SEM photographs of CdS are shown in **Figure 7**. CdS is aggregate particles having rough surface, which were constructed from nanometer sized primary particles. The aggregate particles prepared by electro-spray pyrolysis are finer than those by ultrasonic spray pyrolysis. It is interesting to study further on the size of their primary particles, since the size of electro-spray pyrolysed primary particles seems to be larger than those of ultrasonic spray pyrolysis.

Figure 8 shows TEM photographs of CdS, which also verify the previous results. About 200 particles were picked up randomly from **Figure 8** to evaluate the mean volume diameter of the particles. The results are shown in **Table 2**. As also mentioned in

Fig. 6 X-ray diffraction patterns of CdS particles prepared at different solution concentrations, using ultrasonic (US) and electrostatic (ES) spray pyrolysis, respectively. (Symbol O represents the hexagonal CdS phase)

Fig. 7 SEM micrograph of CdS particles prepared by ultrasonic (US) and electrostatic (ES) spray pyrolysis, respectively. (Solution concentration is 0.05 mol/l)

Fig. 8 TEM micrograph of CdS particles prepared by ultrasonic (US) and electrostatic (ES) spray pyrolysis, respectively. (Solution concentration is 0.01 mol/l)

the previous results, electrospray pyrolysis prepares finer particles than ultrasonic spray pyrolysis method. From these results, the availability of this method to generate the ultrafine particles below $0.1\mu\text{m}$ could be confirmed.

Table 2 Relation between the solution concentrations and the mean volume diameter of CdS particles prepared by ultrasonic (US) and electrostatic (ES) spray pyrolysis, respectively.

Solution concentration [mol/l]	Mean volume diameter [μm]	
	Ultrasonic	Electrostatic
0.001	—	0.056
0.005	0.309	0.058
0.010	0.352	0.090

X-ray diffraction patterns of ZnS particles are shown in **Figure 9** with peaks of the cubic ZnS

Fig. 9 X-ray diffraction patterns of ZnS particles prepared at different solution concentrations, using ultrasonic (US) and electrostatic (ES) spray pyrolysis, respectively. (Symbol O represents the cubic ZnS phase)

phase. Comparing with particles prepared by ultrasonic spray pyrolysis, electrostatic spray pyrolysed particles show broader diffraction peaks. These are similar to CdS case and due to the same reason as its case.

Figure 10 shows TEM photographs of ZnS particles prepared by those two methods. Although there is a broad size distribution, these pictures also verify that electrospray pyrolysis method generates finer ZnS particles than ultrasonic spray pyrolysis. **Figure 11** shows the relation between the solution concentrations and the mean volume diameter of ZnS particles, and also supports the previous tendencies.

It is necessary to predict the droplet diameter generated during the process. In spray pyrolysis,

Fig. 10 TEM micrograph of ZnS particles prepared by ultrasonic (US) and electrostatic (ES) spray pyrolysis, respectively. (Solution concentration is 0.05 mol/l)

Fig. 11 Relation between the solution concentrations and the mean volume diameter of ZnS particles prepared by ultrasonic (US) and electrostatic (ES) spray pyrolysis, respectively.

one sprayed droplet is assumed to change into one dense spherical particle inside the reaction furnace. The following equation can be derived from the relation between one droplet (concentration of the solution, C_s ; volume mean diameter, D_d ; molecular weight, M) and one dense particle (final volume mean diameter, D_p ; theoretical density, ρ_p).

$$D_p = D_d (MC_s / \rho_p)^{1/3} \quad (3)$$

By using Eq. (3), the droplet diameters can be predicted from the generated particle diameters. The prediction results indicate that generation of the droplets with volume mean diameters of 0.8-0.95 μm range are possible.

This study also shows that electrospray pyrolysis can generate particles of about 10 nm. By further adjusting the experimental conditions, it is hoped that relatively large amount of ultrafine particle in this smaller class will be produced practically.

5. Conclusion

On the preparation of metal sulfide fine particles at the same solution concentration the electrospray pyrolysis technique could produce particles smaller by one order of magnitude as compared to ultrasonic spray pyrolysis. Without lowering the solution concentrations, the electrospray could exceed the lower limit of the generation of 0.1 μm fine particles on the spray pyrolysis process. While it was difficult to prepare the particles at that range by the typical (atomizer) spray pyrolysis methods, even the concentration of the starting solution was reduced. It is required further studies to facilitate the effective control of multiple parameters of the electrospray system including the liquid physical properties, as well as their relation to the generated particle sizes.

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Nomenclature

C_s	: solute concentration in starting solution	(mol/l)
D_d	: droplet diameter	(m)
D_p	: particle diameter	(m)
M	: molecular weight of particle	(-)
ρ_p	: density of particle	(kg/m^3)

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Author's short biography

Kikuo Okuyama

Professor Kikuo Okuyama graduated from Dept. of Chemical Engineering in 1971 and from Graduate School of Chemical Engineering in 1973, of Kanazawa University. He received the Doctor degree of Engineering in 1978 from University of Osaka Prefecture. He was appointed to Research Associate in 1973, Assistant Professor in 1984 and Associate Professor in 1986, of Dept. of Chemical Engineering, University of Osaka Prefecture. He has been Professor of Dept. of Chemical Engineering, Hiroshima University, since 1990.

His research interest covers preparation of new material particles and thin films by aerosol methods, analysis of aerosol reactor, development of aerosol size analysis technique, particle contamination control in semiconductor preparation process, gas-to-particle conversion process of polluted gas.

I. Wuled Lenggoro

Wuled Lenggoro studied Chemical Engineering at Hiroshima University and received master degree in 1995. Since then he is a doctorate student of Prof. Okuyama in Department of Chemical Engineering at Hiroshima University.

His current research are the preparation and characterization of fine particles in spray pyrolysis process.

Noboru Tohge

Professor Noboru Tohge graduated from Dept. of Applied Chemistry in 1971 and from Graduate School of Electrical Engineering in 1974, of University of Osaka Prefecture. He received the Doctor degree of Engineering in 1980 from University of Osaka Prefecture. He was appointed to Research Associate in 1974, Assistant Professor in 1986 and Associate Professor in 1989, of Dept. of Applied Chemistry, University of Osaka Prefecture. He has been Professor of Dept. of Metallurgical Engineering, Kinki University, since 1993.

The main fields of his current research activity are the sol-gel processing of advanced thin films and the characterization of spray-pyrolyzed fine-particles.