Korean J. of Chem. Eng., **13**(4), 573-577 (1996)

CONTROL OF PARTICLE SIZE DISTRIBUTION OF ULTRAFINE IRON PARTICLES IN THE GAS PHASE REACTION

Hee Dong Jang†, Kyun Young Park* and Cheong Song Choi*

Div. of Minerals Utilization and Materials, Korea Institute of Geology, Mining and Materials, 30 Kajung dong, Yusung ku, Taejon 305-350, Korea
*Dept. of Chemical Engineering, Kongju National University, 182 Shinkwan-dong, Kongju, Chungnam, 314-701, Korea
**Dept. of Chemical Engineering, Sogang University, 1 Shinsoo-dong, Mapo ku, Seoul 121-742, Korea
(Received 5 March 1996 • accepted 27 August 1996)

Abstract – Experiments on the synthesis of ultrafine iron particles have been made for the control of particle size distribution using the gas phase reduction of ferrous chloride with hydrogen. The previous studies were focused on the control of particle size of ultrafine particles with the variation of the partial pressure of reactants, residence time of feed, and reaction temperature. However, it is also very important to control the size distribution of ultrafine particles. In this study, the control of particle size distribution was investigated from the standpoint of nucleation. The variation of evaporating condition at the same evaporation rate of ferrous chloride, and of the temperature gradient of reactants between preheating zone and reaction zone were adopted as experimental variables. Ultrafine iron particles having uniform size distribution could be produced under the control of evaporating condition such as the change of the surface area at constant evaporating temperature. As the temperature gradient decreased, particle size distribution became uniform and average particle sizes were also decreased.

Key words: Particle Size Distribution, Ultrafine, Iron Particles, Gas Phase

INTRODUCTION

Ultrafine particles of less than 100 nanometer in particle size find many applications as new materials for magnetic tape, catalyst, sensors and sintering additives, etc. [Granqvist and Buhrman, 1976; Tasaki, 1979; Kashu, 1984]. Ultrafine particles show a high surface area per unit volume. This high value causes the increase of activity in catalyst and sensitivity in sensor. Ultrafine iron particle is used for high density recording media and used in sintering additives, etc. Preparation of ultrafine particles by gas phase chemical reaction becomes an important technology because this method is advantageous in easy control of the condition, particle size, particle crystal structure and purity [Kato, 1987].

Synthesis of ultrafine metal particles by gas phase reaction is reported by many researchers [Lamprey et al., 1962; Saeki et al., 1978; Otsuka et al., 1984; Morooka et al., 1987; Ishikawa et al., 1990]. Previous researchers have investigated the effect of variables such as reaction temperature, partial pressure of feed, residence time of feed in reaction zone on the production of ultrafine particles. However, previous results did not focuse on the control of particle size distribution of produced ultrafine particles. Lai et al. [1972] suggested the self-preserving size distribution theory that is attained coagulating aerosols. That theory represents that aerosols having any initial particle size distribution converge same particle size distribution after a sufficiently long time. Their results have been used extensively by many investigators for both theoretical and experimental aerosol studies. Therefore, it was difficult to find the previous experimental results concerned with the control of particle size distribution of particles. However, there were differences between previous experimental results and theoretical results for the particle size distribution because particles produced by reaction did not have a sufficiently long residence time in the aerosol reactor. Lee [1983] and Lee et al. [1984] suggested theoretical results that initial size distribution of aerosols had a rather pronounced effect on the coagulation rate and then played the very important role to the final size distribution of aerosols. However, there was no experimental result on the effect of initial size distribution.

The purpose of this study is to investigate the effects of the initial distribution of reactant on the final particle size and distribution of produced ultrafine particles experimentally. However, it was impossible to detect the initial distribution of reactant directly during the vapor phase synthesis of ultrafine particles. Therefore, we adopted indirect method. For the indirect method, two experimental variables were chosen as follows; variation of evaporating temperature in the same evaporation rate of ferrous chloride, and temperature gradient of reactants between preheating zone and reaction zone.

EXPERIMENTS

1. Apparatus

A schematic drawing of experimental apparatus is shown in Fig. 1. It consists of gas purification, reaction, particles collection and off-gas treatment part, and data acquisition and control part by computer. Argon gas (99.999%) is injected as a carrier gas to reactor through a column packed with copper particles (20/30 mesh) and heated at 400°C and gas purifier (Ham-

†To whom all correspondences should be addressed.

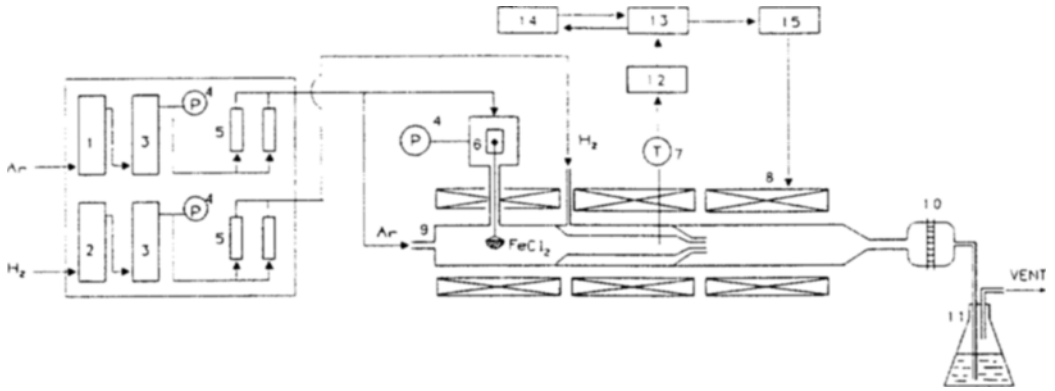


Fig. 1. Schematic diagram of experimental apparatus.

1. Copper powder column	2. O_2 removing purifier	3. Gas purifier	4. Pressure indicator	5. Flowmeter
6. Load cell	7. Thermocouple	8. Tube furnace	9. U. F. P. reactor	10. Powder collector
11. HCl absorber	12. Amplifier	13. A/D, D/A converter	14. Computer	15. SCR

mond Drierite Co.) in which $CaSO_4$ particles and molecular sieve are main components.

A multi-stage aerosol reactor was made of quartz tube and was consisted of evaporation for $FeCl_2$, preheating of $FeCl_2$ vapor and H_2 gas, and reaction part where reactants meet. The reactor was 155 cm long, each length of evaporation and preheating zone was 40 cm, and that of reaction part is 75 cm. The inside diameter of evaporation zone was 5.0 cm, and $FeCl_2$ was loaded in quartz boat connected with load cell for the measuring of weight change. Preheating part for reactants was composed of double pipe, the diameter of inner tube was 3.0 cm and that of outer tube was 5.0 cm. Argon gas and $FeCl_2$ vapor flow through the inner tube, and H_2 gas flows through the outer tube. The nozzle for the mixing of reactants was installed before the reaction part. The diameters of inner and outer nozzles were 1.2 cm, 2.0 cm, respectively and their length of nozzle were all 10 cm. The diameter of reaction tube was 3.0 cm and length was 75 cm. The temperature of each zones in reactor was measured by a K-type thermocouple, and the tube furnace is composed of four pieces of heater of which temperature is controlled separately by computer. The first one was for evaporation, the second one was for preheating, and the third and the fourth ones were used to control the axial distribution of reaction temperature.

Produced ultrafine particles were collected by using teflon membrane filter which has a 20 micrometer in average pore size.

2. Procedure

The reactor was purged by argon gas to make an inert atmosphere in the reactor. The furnaces were heated while Ar gas was flowed into the reactor. Temperature of each zone in the reactor was controlled by a computer. For the removal of water in the $FeCl_2$, furnace in the evaporation zone was heated until the reactant connected with load cell showed no change in weight. Ar and H_2 gas are purged at a flowrate of 5 *l*/min each after the furnaces were heated to predetermined temperature of each zone. Then $FeCl_2$ was evaporated with constant evaporation rate. The vaporized $FeCl_2$ and H_2 gas were heated to a predetermined temperature through a double pipe in the preheating zone. Then two reactants were allowed to be contacted with each other on leaving a concentric nozzle in the reaction zone.

3. Analysis

For the measurement of particle shape, size and distribution, TEM (transmission electron microscope, Philips Co. Model CM 12) was used. The particle size and distribution were determined by counting more than 500 particles from TEM pictures [Kato, 1987]. The geometric standard deviation which represents the particle size distribution of the particles was obtained by log-probability plot [Stockham and Fochtman, 1978].

RESULTS AND DISCUSSION

1. Effect of Evaporating Condition at the Constant Evaporation Rate of $FeCl_2$

Ferrous chlorides vapor in the evaporating zone has a range of molecular clusters of different sizes when it meets with carrier gas at different situations of the evaporation [Friedlander, 1977; Hinds, 1982]. The $FeCl_2$ vapor reacts with hydrogen in the reaction zone through preheating zone, and then Fe clusters having some size distribution could be produced. The big Fe clusters among them grows into nuclei faster than small clusters. This means that the big clusters grow into particles faster than small ones. If the Fe vapor has a uniform size distribution of clusters, all the clusters will have same growth rate and then uniform particle in size could be produced. Therefore, it is very important to control the initial size distribution of $FeCl_2$ cluster for the synthesis of uniform particles.

We investigated the effect of initial size distribution of $FeCl_2$ and proposed two possible ways to control the initial size distribution of $FeCl_2$ clusters by varying the evaporation conditions of reactant as follows;

(A) change of the evaporation temperature at constant surface area.

(B) change of the surface area at constant evaporation temperature.

The schematic diagram of the two case is shown in Fig. 2. The evaporation rate of $FeCl_2$ is kept same constant in the both cases. In the case of (A), flux of $FeCl_2$ vapor increases as the evaporation temperature increases. Then, the local density of $FeCl_2$ vapor increase and there are high probability of col-

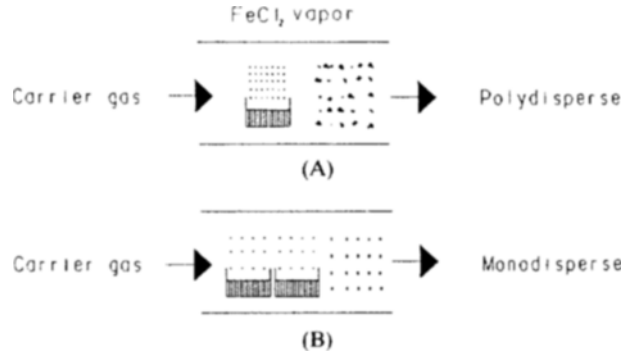


Fig. 2. Schematic diagram on the control of the evaporating conditions.

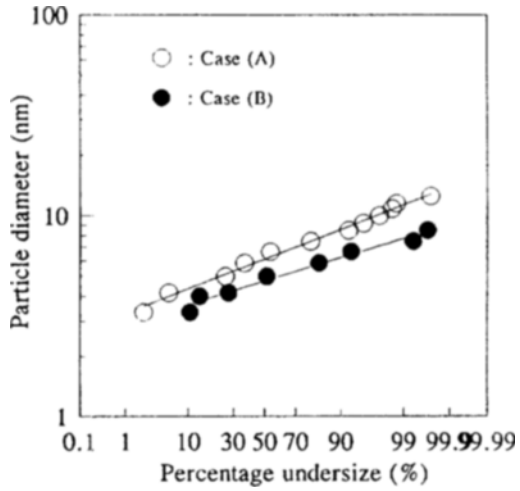


Fig. 3. Log-probability plots of iron particles with different evaporating conditions at the same evaporation rate (0.008 g/min).
[Case (A); Evaporation temp.: 700°C, Preheating temp. & Reaction temp.: 900°C, Gas flowrate: 10 *l*/min
Case (B); Evaporation temp.: 660°C, Preheating temp. & Reaction temp.: 900°C, Gas flowrate: 10 *l*/min].

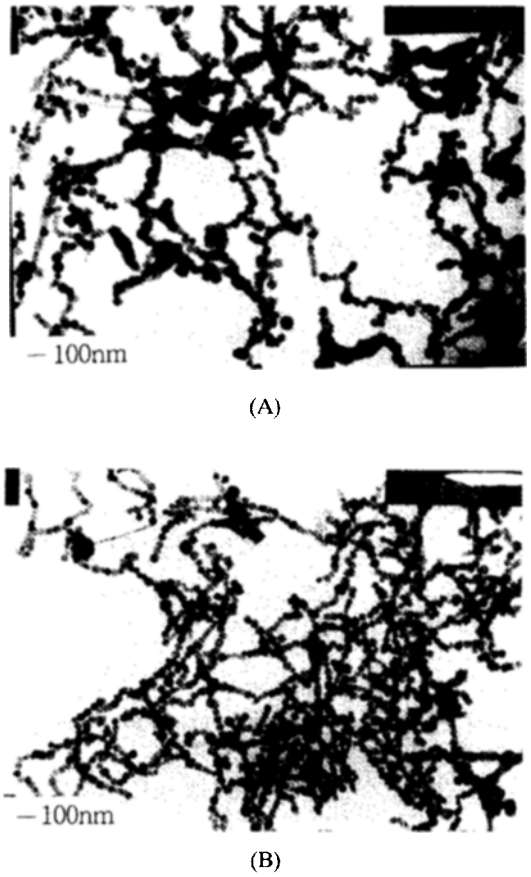


Fig. 4. Transmission electron microscopic images of the iron particles with different evaporating conditions at the same evaporation rate.

lisions between $FeCl_2$ molecules. Therefore, clusters of different size will be dominantly formed. However, in the case of (B), the local density is kept constant since the flux of $FeCl_2$ evaporation does not change at all. Then, clusters in the case of (B) is more uniform in distribution than cluster in the case of (A). Therefore, the smaller and more unifrom particles may be produced due to homogeneous reaction of uniform distribution of $FeCl_2$ cluster. The experiments considering such concepts were made at the condition of the same preheating and reaction zone temperature, and constant gas flowrate. Iron particles were obtained with different evaporating conditions at the same evaporation rate of $FeCl_2$. Fig. 3 and 4 shows the log-probability plot which represents the size distribution of particles at different evaporating conditions, and images of iron particles, respectively. There were differences in particle size and size distribution of two different evaporating conditions. Particles obtained at the condition of (B) were smaller and more uniform in size than the particles of condition (A). Therefore, we conclude that particles of uniform size distribution are produced from the uniform clusters of $FeCl_2$.

We have made another experiments to investigate the variation of particle size and size distribution by increasing the evaporating surface area at the constant evaporating temperature. As the evaporation rate increased with the increase of evaporating surface area at constant temperature, average particle size of produced iron particles was increased and particle size distribution became more uniform (Fig. 5). Therefore, the control of the size distribution of cluster during the evaporation of reactant was found as a very important factor in controlling the particle size and size distribution.

2. Effect on the Temperature Gradient of Reactants between Preheating Zone and Reaction Zone

Ferrous chlorides vapors evaporated at constant evaporating condition are carried through preheating zone into the reaction zone for the reduction with hydrogen. The temperature gradient of reactants between preheating zone and reaction zone is very important from the viewpoint of nucleation in the gas phase reaction because nucleation is very sensitive function of temperature. Such temperature gradient also affects the particle size and size distribution during the gas phase reaction [Jang, 1995]. Therefore, two cases of temperature gradient at the condition of constant evaporation rate of $FeCl_2$ and gas flow rate were considered from the standpoint of nucleation as follows;

(C) : reactants are injected at the temperature of 750°C to the

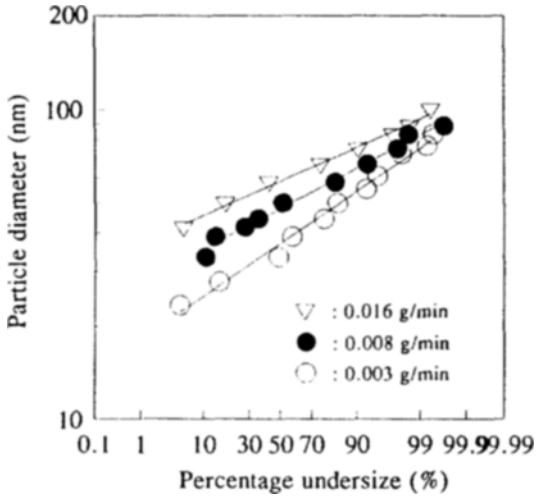


Fig. 5. Log-probability plots of the iron powders with different evaporation rate at the same evaporation temperature (660°C).
(Reaction temp.: 900°C, Gas flow rate: 10 *l*/min, Preheating temp.: 900°C).

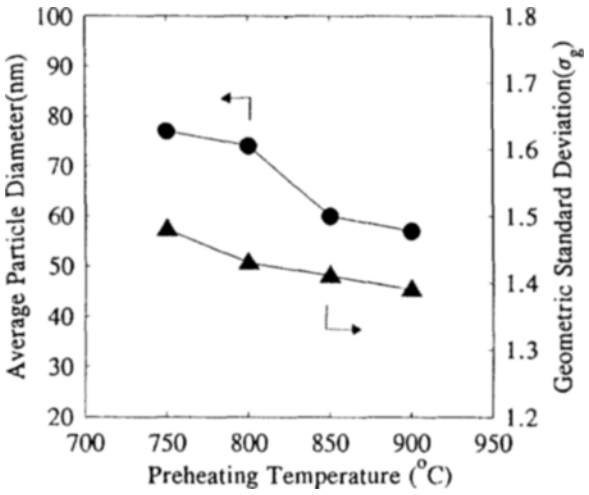


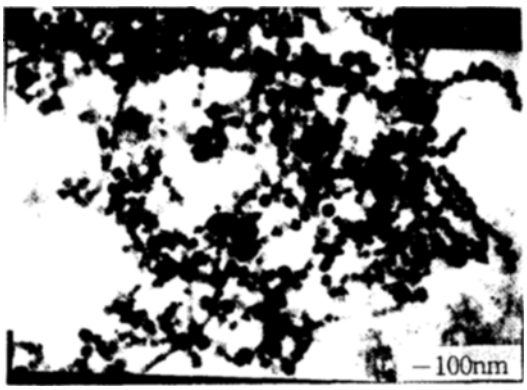
Fig. 6. Effect of preheating temperature on the particle size and size distribution.
(Reaction temp.: 900°C, $FeCl_2$ feedrate: 0.02 g/min, Gas flowrate: 10 *l*/min).

reaction zone at the temperature of 900°C.

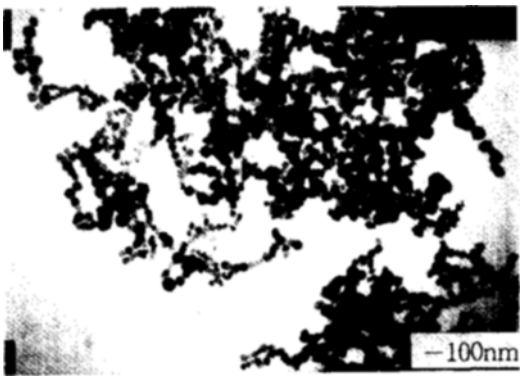
(D) : reactants are injected at the temperature of 900°C to the reaction zone at the temperature of 900°C.

In the case of (C), some of these reactants react at low temperature, so some particles are produced at low temperature (750°C). Such particles play a role as seeds when the nucleation occurred at the zone of the determined reaction temperature (900°C) and also grow until temperature of reactants reaches to the determined reaction temperature (900°C). Then there exists large particles from nucleation in the low temperature and small particles from nucleation in the high reaction temperature. Therefore, it is difficult to obtain uniform particles under this condition. The nucleation in the gas phase production of particles has been generally considered as a homogeneous nucleation. But in the case of (C), it is difficult to consider a homogeneous nucleation at the point of determined reaction temperature. However, in the case of (D), reactants meets together at the determined temperature (900°C), and the homogeneous nucleation without any particles produced at the lower temperature (750°C) will occur. The particles would also have less time to grow than in case (C), so their average size would be smaller. Therefore, more uniform and smaller particles could be obtained in the case of (D) than the particles in the case of (C).

The effects of temperature gradient in the above cases were investigated by varying preheating temperatures of reactants at constant reaction temperature experimentally. Fig. 6 shows the effects of temperature gradient between preheating zone and reaction zone on the particle size and distribution of ultrafine iron particles in the gas phase reaction. As the preheating temperature approached the reaction temperature, i.e., temperature gradient decreased, average particle size of iron particles was decreased, and particle size distribution became more uniform. Fig. 7 also shows the images of both case of (C) and (D). From Fig. 6 and 7, we confirm that the control of temperature gradient play an important role in the particle size and size distribution of ultrafine iron particles in the gas phase synthesis.



(C)



(D)

Fig. 7. Transmission electron microscopic images of the iron particles with different temperature gradient.

CONCLUSION

The synthesis of ultrafine iron particles for the control of par-

ticle size distribution was carried out in the gas phase reduction of $FeCl_2$. Effects of evaporating methods at the constant evaporation rate of $FeCl_2$ and of temperature gradient between preheating zone and reaction zone were investigated for the control of particle size distribution of iron particles. Ultrafine iron particles of uniform size distribution were obtained under the change of the surface area of reservoir at constant reservoir temperature. As the temperature gradient decreased, particle size distribution became more uniform, and particle sizes were also decreased. Therefore, variation of evaporating method at the constant evaporation rate of $FeCl_2$, and of temperature gradient between preheating zone and reaction zone in the reactor were found to be very important factors in controlling the particle size and size distribution.

ACKNOWLEDGMENT

This research was supported by the Korea Ministry of Science and Technology. The authors acknowledge financial support of Korea Ministry of Science and Technology.

REFERENCES

Friedlander, S. K., "Smoke, Dust and Haze", Wiley, New York (1977).

Granqvist, C. G. and Buhrman, R. A., "Ultrafine Metal Particles", *J. Appl. Physics*, **47**, 2200 (1976).

Hinds, W. C., "Aerosol Technology", Wiley, New York (1982).

Ishikawa, H., Otsuka, K., Nitta, M. and Yonehana, Y., "Preparation of Ultrafine Particles by Hydrogen Reduction of Chloride Vapors", *Kawasaki Steel Tech. Report*, **23**, 41 (1990).

Jang, H. D. and Jeong, J., "Effects of Temperature on Particle Size in the Gas Phase Production of TiO_2", *Aersol Sci. and Tech.*, **23**, 553 (1995).

Kashu, S., "Ultrafine Metal Particles", *Chem. Eng. Japan*, **4**, 45 (1984).

Kato, A., "Vapor Synthesis of Ceramic Powders", *Advanced in Ceramics*, **21**, 181 (1987).

Lai, F. S., Friedlander, S. K., Pich. J. and Hidy, G. M., "The Self-Preserving Particle Size Distribution for Brownian Coagulation in the Free-Molecule Regime", *J. Colloid Interface Sci.*, **39**, 395 (1972).

Lampry, H. and Riply, R. L., "Ultrafine Tungsten and Molybdenum Powders", *J. Electrochem. Soc.*, **109**, 713 (1962).

Lee, K. W., "Change of Particle Size Distribution During Brownian Coagulation", *J. Colloid Interface Sci.*, **92**, 315 (1983).

Lee, K. W., Chen, H. and Gieske, J. A., "Log-Normally Preserving Size Distribution for Brownian Coagulation in the Free-Molecule Regime", *Aersol Sci. and Tech.*, **3**, 53 (1984).

Morooka, S., Kobata, A., Yasutake, T., Ikemizu, K. and Kato, Y., "Size of Nickel and Molybdenum Fine Particles Produced by Gas Phase Reaction", *Kagaku Kogaku Robunshu*, **13**, 481 (1987).

Otsuka, K., Yamamoto, H. and Yosizawa, A., "Preparation of Fine Particles Applications", *Jpn. J. Chem.*, **6**, 869 (1984)

Saeki, Y., Matsuzaki, R., Nishihara, H. and Aoyama, N., "Preparation of Cobalt Powder by Hydrogen Reduction of Cobalt Dichloride", *Denki Kagaku*, **46**, 643 (1978).

Stockham, J. D. and Fochtman, E. G., "Particle Size Analysis", Ann Arbor Science, Michigan (1978).

Tasaki, A., "Metal Tape Using Ultrafine Powder Prepared by Gas Evaporation Method", *IEEE Trans. Mag.*, **15**, 1540 (1979).