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Preparation of nanometre size oxide particles using filter expansion aerosol generator

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Crystalline zinc oxide particles of nanometre size (< 20 nm) particles were produced from a zinc acetate solution by using a filter expansion aerosol generator (FEAG). The FEAG is an aerosol generator that is operated at 60 torr reactor pressure and produces droplets of around 2 μm. The shape of the particles produced by the FEAG were distinctively different from those produced by the ultrasonic spray source (USS). Results from scanning electron microscopy (SEM) and X-ray diffractometry (XRD) indicated that crystalline zinc oxide particles of nanometre size were produced at 600 °C in 0.02 s residence time. Weight loss of these particles, determined by thermogravimetric analysis (TGA), was 3 wt%. Based on the morphology change as a function of the reactor temperature and solute concentration, we proposed that the nanometre particles were formed by uniform precipitation at the drying stage and decomposition followed by disintegration into nanometre particles. It was also shown that exothermic decomposition of the solute was not required for the disintegration of the primary particles in the FEAG process. This result opened up an opportunity for producing carbon-free nanometre particles from nitrate salts by using the FEAG.

1. Introduction

Nanometre size particles have unique properties such as high reactivity [1], low sintering temperature [2] and superplasticity [3]. The nanometre particles have been prepared by spray pyrolysis [4, 5], inert gas condensation [6], wet chemical method [7, 8], sputtering [9], microwave plasma synthesis [10] and the two-step process of Gleiter [11].

Among these methods, the spray pyrolysis is an attractive method for preparing nanometre size particles because of its high production rate, continuous operation, and simple apparatus.

Spray pyrolysis is a method of producing particles, in which a misted stream of precursor solution is dried, precipitated, and decomposed in a tubular furnace reactor. The size and morphology of particles are mainly determined by the type of aerosol generators. This method has been used to form a wide variety of materials in powder form, including metals, metal oxides, non-oxide ceramics, superconducting materials, and nanophase materials [12].

Particles produced by spray pyrolysis are more uniform in size and composition than those produced by other techniques because of the microscale reaction within a droplet and the lack of a milling process. Additionally, multicomponent materials are easily made by spray pyrolysis. Each droplet contains precursors in the same stoichiometry as desired in the product.

But, preparation of nanometre particles by spray pyrolysis has been reported only for a few cases and the formation mechanism is not well understood. Sproson and Messing [4] showed that powder morphology was dependent upon the precursor salt in spray pyrolysis. Hard, spherical, aggregated ZnO, MgO, Mn_3O_4 and NiO particles were prepared from zinc nitrate, magnesium nitrate, manganese acetate and nickel acetate solutions while fine-grained, aggregate-free powders were obtained from zinc acetate and magnesium acetate solutions. This difference was explained in terms of the decomposition behaviour of the individual salts.

González-Carreño *et al.* [5] prepared nanometre size γ-Fe_2O_3 particles from various iron salt solutions by spray pyrolysis. Aggregated particles of γ-Fe_2O_3 with average diameter of 6 nm were obtained from nitrate solutions, whereas, γ-Fe_2O_3 obtained from acetylacetonate solution consisted of monodisperse particles of about 5 nm in diameter. They showed that monodisperse nanometre particles were formed due to the explosion of acetylacetonate precursors, for which the exothermic decomposition of the salt precursor was responsible.

Kang and Park [13] proposed a new aerosol generator, named as the filter expansion aerosol generator (FEAG), that can be applied to the preparation of particles and thin films under reduced pressure. The FEAG consists of a pneumatic nozzle, a porous glass filter, and a vacuum pump. Liquid is sprayed through a pneumatic nozzle on to a glass filter surface using a carrier gas, where it forms a thin liquid film. This liquid film is pressed through the filter pores by the carrier gas and expanded into a low pressure chamber.

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The advantage of the FEAG process for the preparation of ultrafine particles is its capability of producing a large quantity of liquid droplets, and also this aerosol generator, in principle, can be scaled up by increasing the vacuum pump capacity and filter area. The disadvantage of this process for the preparation of ultrafine particles is the difficulty of recovering the particles due to the low pressure.

In this paper, we report a method of preparing nanometre size ZnO and other metal and oxide powders by FEAG. The formation mechanism of nanometre size particles in the FEAG process was identified. The powder characteristics of the FEAG process was compared with those of ultrasonic spray pyrolysis.

2. Experimental details

The experimental apparatus, the FEAG, used in this work is shown in Fig. 1, of which details are described elsewhere [13]. Metal salt solution is atomized into droplets of 2 μm at 5 ml min^{-1} and delivered into a hot-wall reactor at 60 torr. As the aerosol stream passes through the reactor, solvent evaporates and metal salt decomposes to form product particles. At the end of the reactor, a powder collection filter, a liquid nitrogen trap, and a vacuum pump of 600 l min^{-1} capacity are connected in series. In order to compare the morphology of the FEAG-produced particles with ultrasonic spray pyrolysis, an ultrasonic spray source (USS) was connected in place of the FEAG. Characteristics of these two aerosol generators used in this study was listed in Table I.

Zinc oxide, silver and other oxide particles were prepared by pyrolysing droplets produced by the FEAG and ultrasonic aerosol source. Precursor salts were zinc acetate, silver nitrate, manganese acetate, palladium nitrate and copper nitrate. The reactor temperature was maintained isothermally at between 200 to 800 °C. Residence time in the FEAG process ranged between 0.02 to 0.04 s depending on the reactor temperature. Residence time in ultrasonic spray pyrolysis was ranged between 1 to 2 s at 10 l min^{-1} air flow rate. The concentration of solution was varied between 0.02 to 0.75 M.

The prepared particles were characterized with X-ray diffractometry (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results and discussion

3.1. Characterization of ZnO particles generated from the FEAG process

Shapes of ZnO particles prepared at 200, 250, 300, 350, 400 and 600 °C by using the FEAG are shown in Fig. 2. The concentration of zinc acetate solution was 0.1 M and reactor pressure was maintained at 60 torr.

At 200 °C (Fig. 2a), the particles were round with a smooth surface and had no precipitated secondary particles because only slow drying dominated. From 250 °C (Fig. 2b), the primary particles began to disintegrate into the secondary nanometre particles. But the primary particles kept their original round shapes up to 300 °C (Fig. 2c), which was a high enough temperature for droplets to be completely dried. It should be noted that, over such a short residence time (less than 0.04 s), there was not enough gas coming off from the decomposition of zinc acetate because the zinc acetate was decomposed to form zinc oxide crystal at the reactor temperature of 300 °C (Fig. 2c), as indicated from the XRD spectrum (Fig. 3, 300 °C). Therefore, we concluded that secondary particles were precipitated at the drying stage and were composed of zinc acetate salt and a small fraction of zinc oxide.

At 350 °C (Fig. 2d), which is a high enough temperature to dry particles completely and decompose them to some extent, the primary particles began to

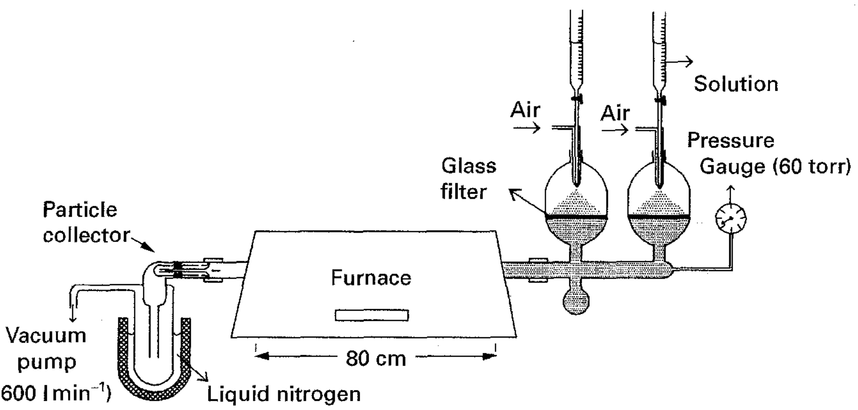

Figure 1 The schematic diagram of FEAG process.

TABLE I Comparison of the FEAG and ultrasonic aerosol generators used in this experiment

Aerosol generator	Mean droplets size (μm)	Standard deviation of droplets	Feed flow rate (ml min^{-1})	Pressure (torr)
FEAG	2.1	1.76	5	60
Ultrasonic	5.8	0.97	1	760

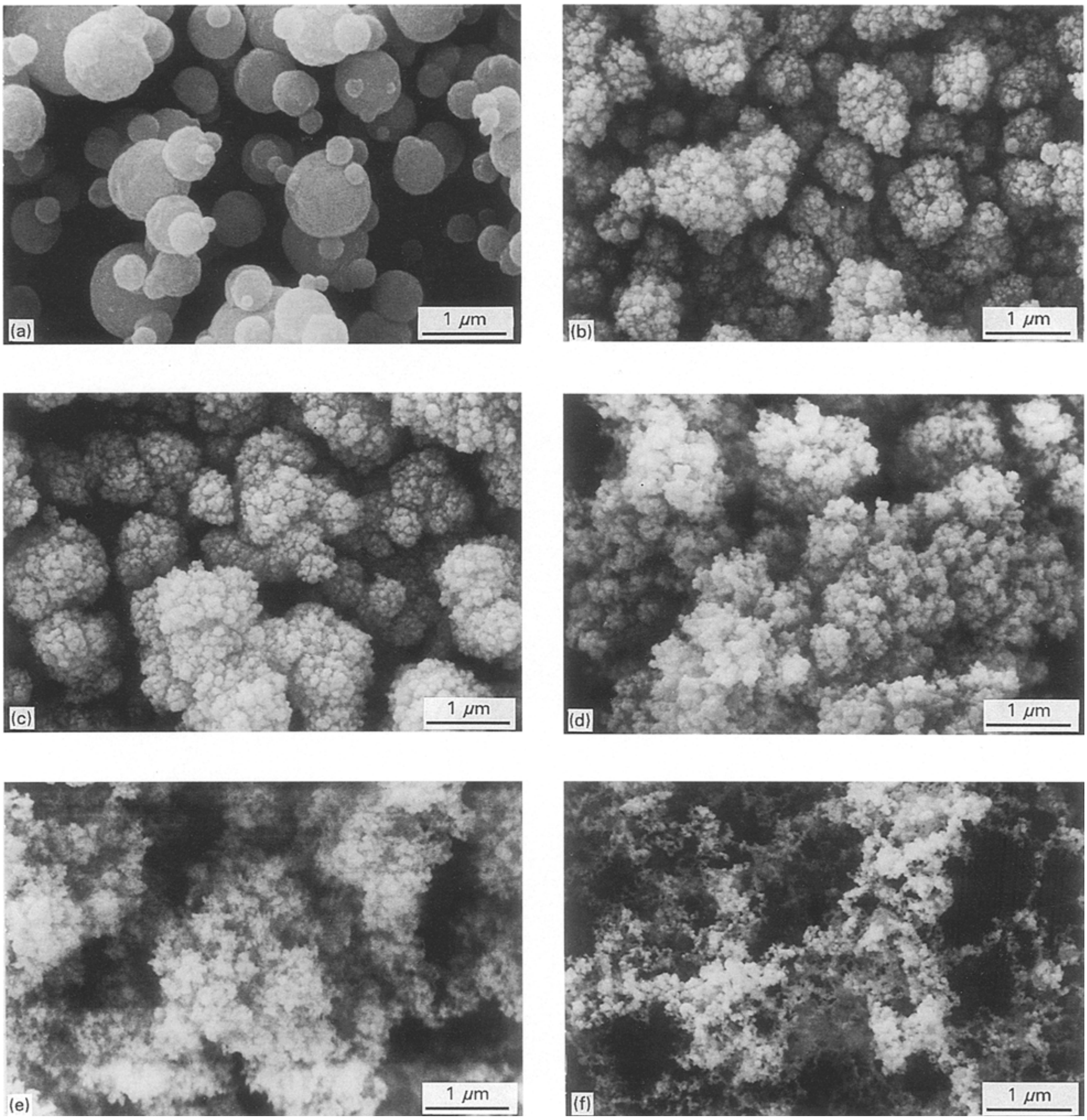

Figure 2 SEM photographs of ZnO particles prepared at different temperatures by the FEAG process (0.1 M zinc acetate, 60 torr).

lose their identity. At 400 °C (Fig. 2e), the original round shapes of the agglomerates had completely disappeared and fragmented into nanometre size crystalline ZnO particles. Gas evolved from the decomposition of zinc acetate is believed to make the bounded particles fragment into nanometre ZnO particles. From 500 °C, all characteristic peaks of zinc oxide crystal, as shown in Fig. 3 (500 °C), began to be distinct and turned into intense peaks at 600 °C (Fig. 3, 600 °C).

Fig. 4 shows the TEM micrographs of ZnO particles prepared from 0.5 M zinc acetate solution at 400 and 800 °C. The particles prepared at 400 and 800 °C have monodisperse size distributions and mean size of particles measured from the TEM micrographs are 8 and 20 nm, respectively.

In Fig. 3, the sharpness of the XRD peak is increased as the preparation temperature increases. Therefore, the particles prepared at a lower temperature have the smaller mean particle size. This result is consistent with that of the TEM micrographs shown in Fig. 4.

At 600 °C, according to the TGA result (Fig. 5), the weight loss of these ZnO particles was only 3 wt%. Therefore, 600 °C is a high enough temperature to complete the decomposition of zinc acetate salt and crystallization in spite of the short residence time (0.02 s) of the FEAG process.

Fig. 6 shows the effect of solute concentration on the particle morphology. Regardless of the solute concentrations, monodisperse nanometre size particles were formed. This result confirms that the secondary nanometre particles were formed at the drying stage and disintegrated into individual particles as the reactor temperature increases.

3.2. Comparison of particles produced by FEAG process and ultrasonic spray pyrolysis

Typical shapes of ZnO particles prepared at 200, 250, 300, 350, 400 and 600 °C by using ultrasonic spray source (USS) are shown in Fig. 7. The concentration of zinc acetate solution was 0.1 M. At 200 and 250 °C (Fig. 7a and b), it is evident that the particles of around 1 μm diameter are hollow and crumpled. Comparing the shapes of these particles with Fig. 2a and b produced by using the FEAG, the initial drying stages of FEAG and USS are different. According to Jayanthi *et al.* [14], hollow particles are formed if the drying rate is fast because solutes do not have enough time to diffuse in and only the surface of the droplet reaches

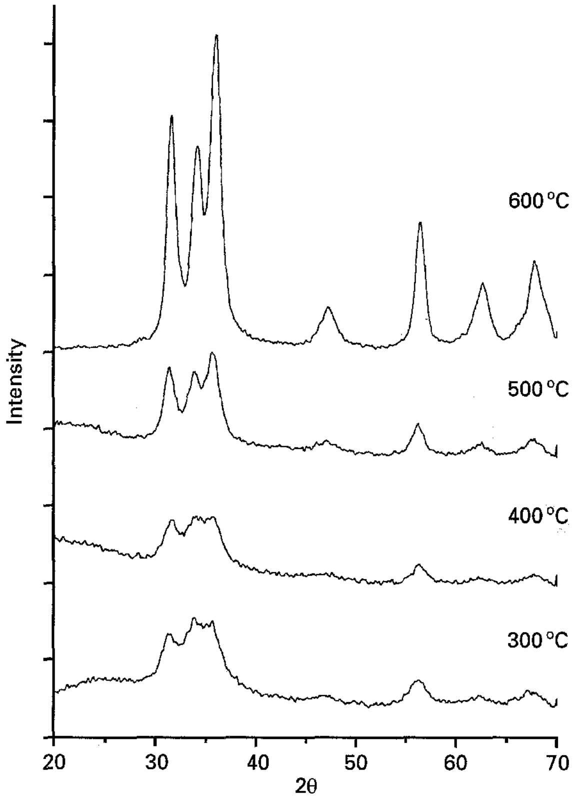

Figure 3 XRD spectra of ZnO particles prepared at different temperatures by the FEAG process (0.1 M zinc acetate, 60 torr).

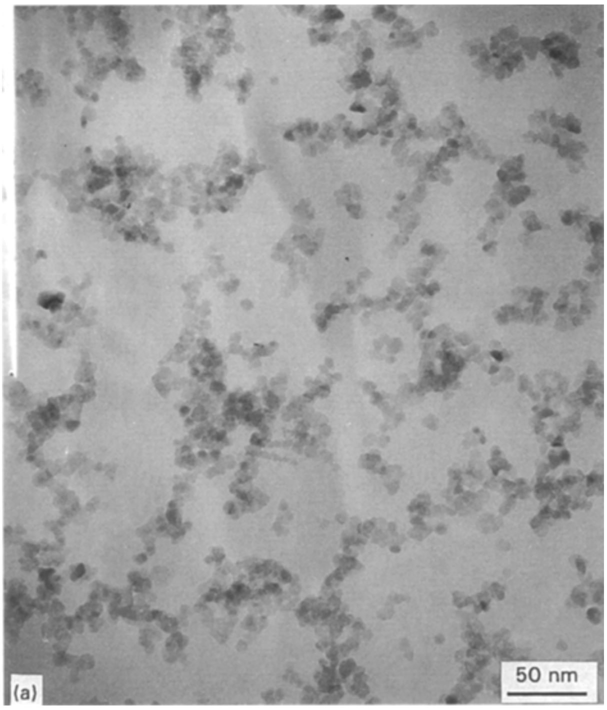

Figure 4 TEM micrographs of ZnO particles prepared by the FEAG process from 0.5 M zinc acetate solution at 400 and 800 °C.

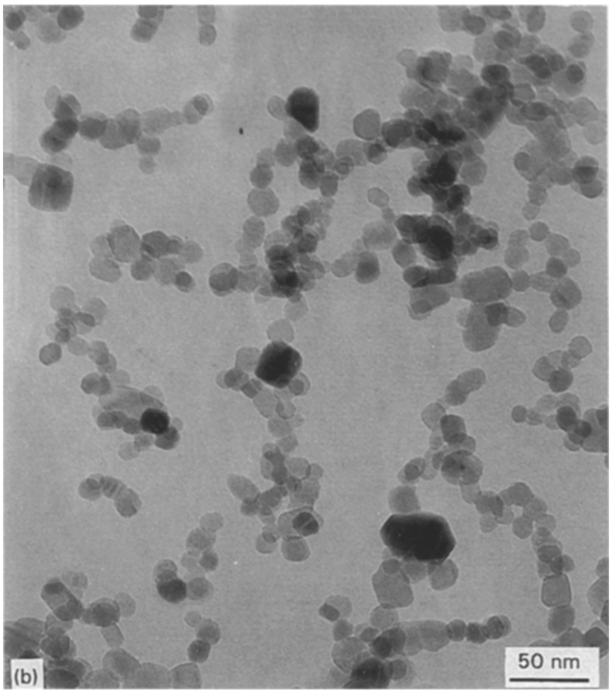

Figure 4 Continued.

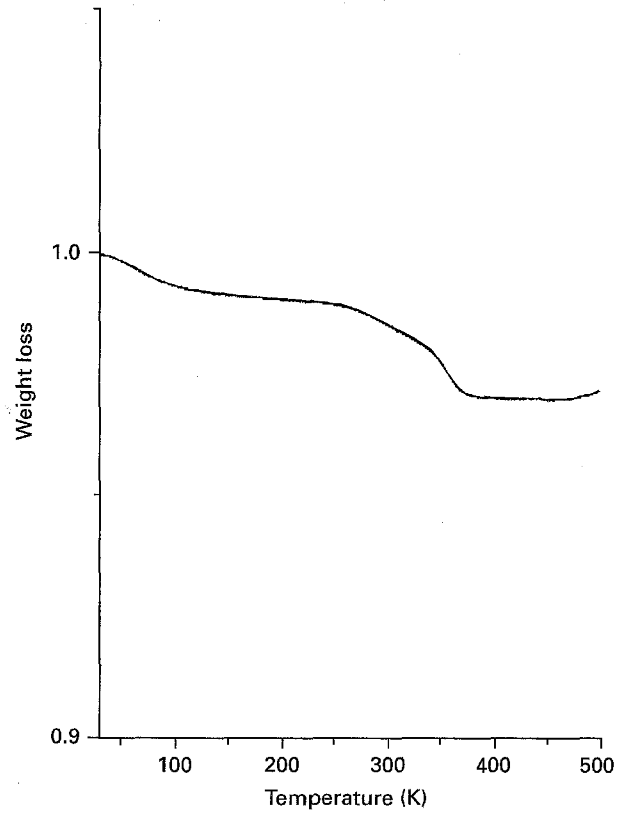

Figure 5 TGA curve of ZnO particles prepared by the FEAG process (0.1 M zinc acetate, 600 °C, 60 torr).

a supercritical saturation concentration. Thus, judging from Fig. 7a and b and Fig. 2a and b, the drying rate in the USS is apparently much faster than in the FEAG. Considering the reactor pressure and droplet size difference of the two aerosol generators, the FEAG-produced droplet should evaporate faster than the USS-produced one. Therefore, the evaporation rate difference does not account for the morphology

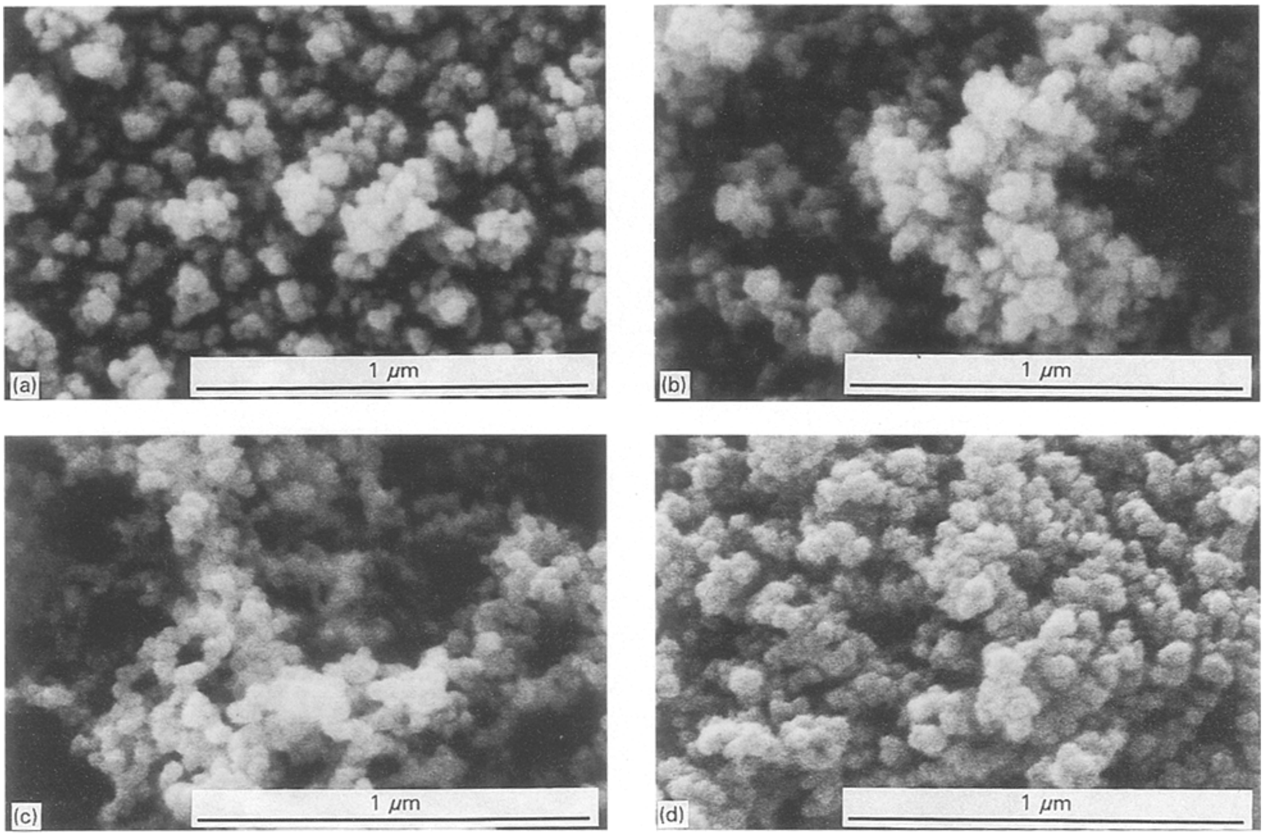

Figure 6 SEM photographs of ZnO particles prepared at different concentrations by the FEAG process (zinc acetate, 600 °C, 60 torr).

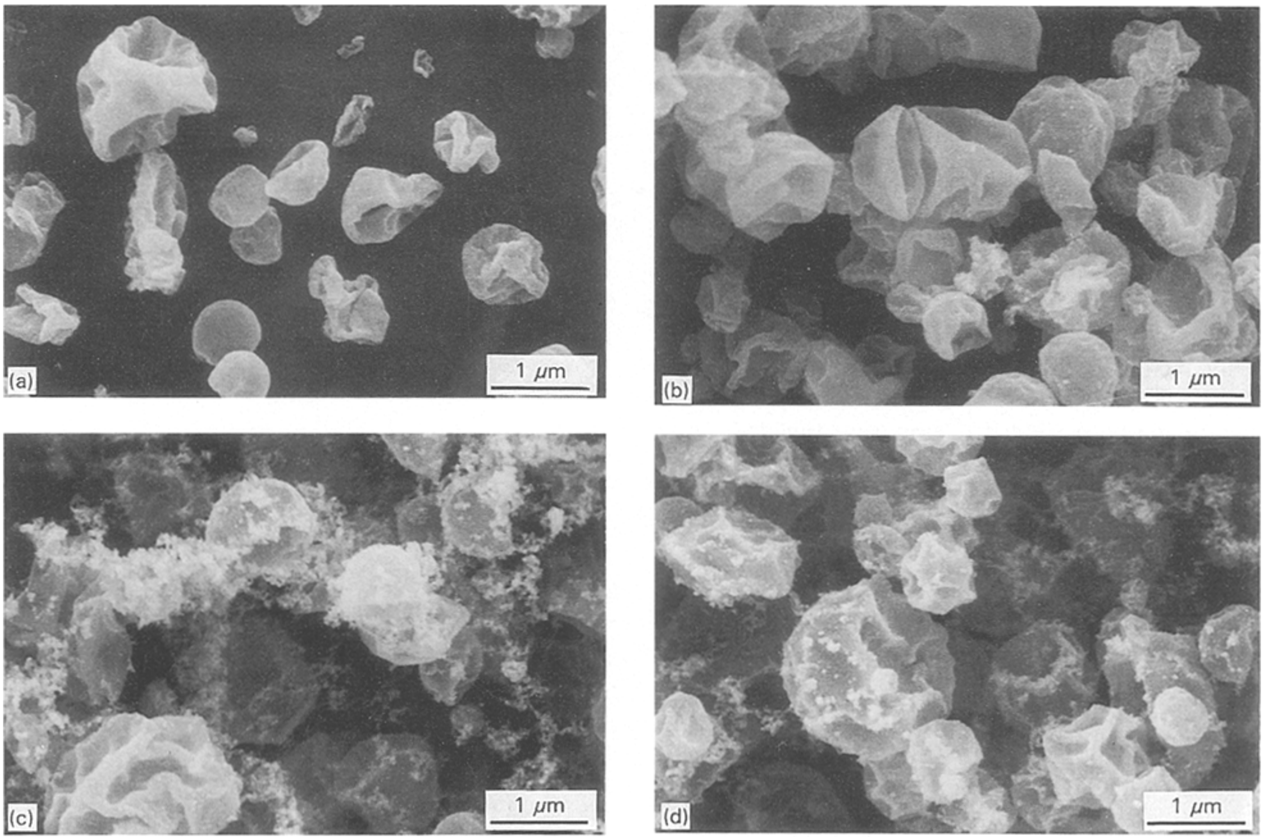

Figure 7 SEM photographs of ZnO particles prepared at different temperatures by ultrasonic spray pyrolysis (0.1 M zinc acetate, 760 torr).

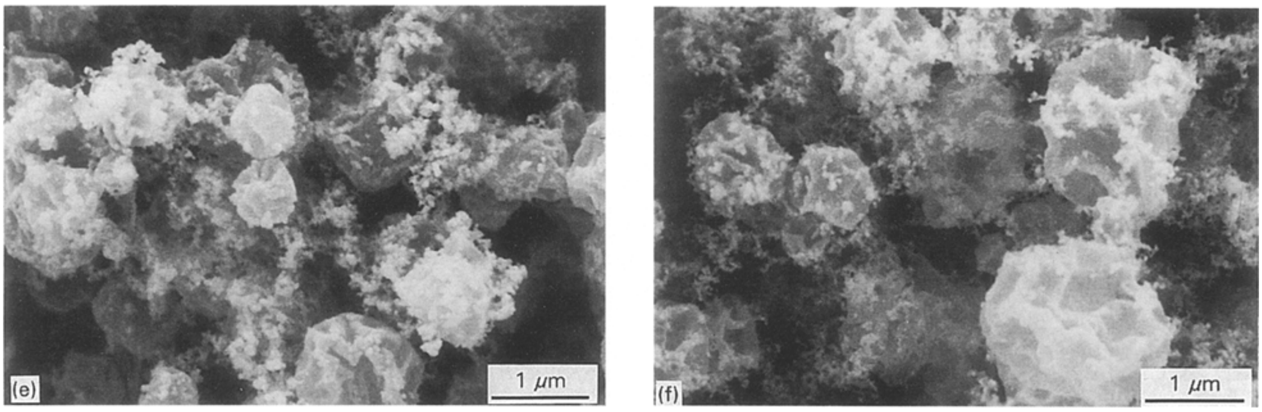

Figure 7 Continued.

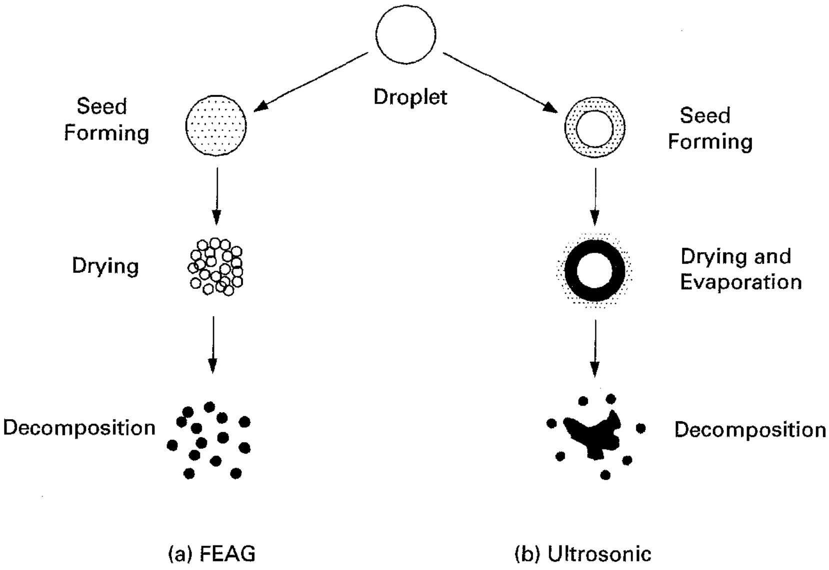

Figure 8 The different ZnO particles formation mechanisms at different processes.

difference of the two generators. Drying of a droplet at reduced pressure requires further investigation.

Above 300 °C (Fig. 7c), several tens of nanometre particles and 1 μm size of bimodal distribution was obtained. The tendency toward bimodal distribution was increased with reactor temperature and had no signs of fragmentation of micrometre size particles. Liu *et al.* [15] also obtained ZnO particles of bimodal distribution by ultrasonic spray pyrolysis at high zinc acetate concentration. They proposed that this bimodal distribution resulted from the evaporation of volatile zinc acetate salt. Comparing Fig. 2c–e with Fig. 7c–e, we see that the FEAG process gives better controlled morphology and smaller particles than the ultrasonic spray pyrolysis method. It should be noted that no sign of explosion of hollow particles were observed from the SEM photographs.

Based on these results, we propose a particle formation mechanism in the FEAG process as shown in Fig. 8. For comparison, formation mechanism in the ultrasonic spray pyrolysis was also drawn in parallel. In the FEAG process, a liquid droplet is evaporated and precipitated uniformly before the shell crust forms. The primary particles, of which the size is determined by the droplet size, are composed of the secondary nanometre particles which are formed at the drying stage. But they do not disintegrate until the decomposition of the solute starts to occur as the droplet temperature increases. Gas evolved from the solute decomposition is believed to contribute to the disintegration. In the ultrasonic spray pyrolysis process, however, rapid drying makes it easy to form a shell crust at the initial drying stage. Evaporation of the solute contributes to the formation of secondary particles. The shapes of particles are hollow and collapsed, and they have a bimodal size distribution.

3.3. Silver particles formation in FEAG process and ultrasonic spray pyrolysis

Difference between the FEAG process and the ultrasonic spray pyrolysis was found to be distinct in the case of preparing silver particles from silver nitrate solution.

Figs 9 and 10 show the SEM photographs of silver particles prepared by ultrasonic spray pyrolysis and FEAG process at 800 °C from 0.04 M silver nitrate solution. The particles made from ultrasonic spray pyrolysis have a spherical shape and mean particle size is 0.47 μm. In this process, one solid particle was formed from one droplet of silver nitrate solution. On the other hand, silver particles formed in the FEAG

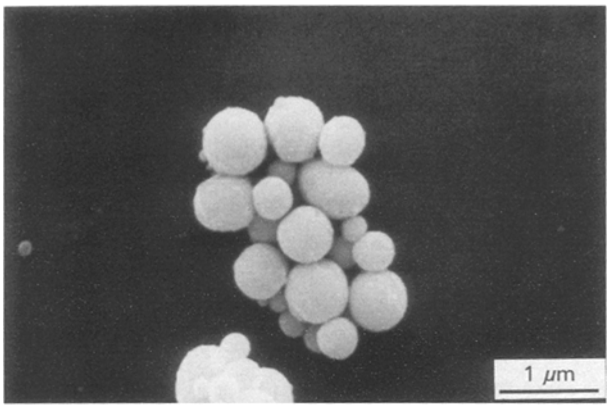

Figure 9 SEM photograph of silver particles prepared by ultrasonic spray pyrolysis (0.04 M silver nitrate, 800 °C, 760 torr).

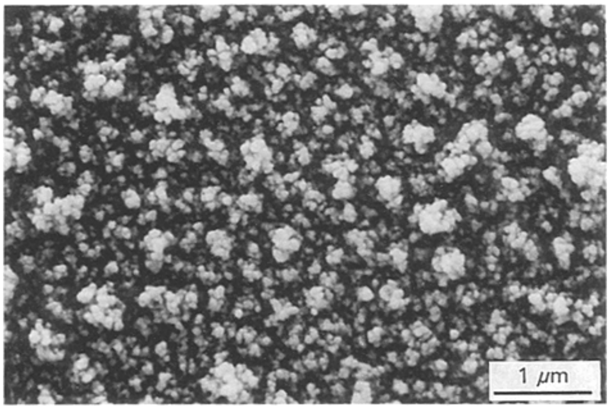

Figure 10 SEM photograph of silver particles prepared by the FEAG process (0.04 M silver nitrate, 800 °C, 60 torr).

process is spherical and the mean particle size is about 60 nm according to the SEM image. These nanometre silver particles were formed by disintegration of the dried primary particles.

Sproson and Messing [4] showed that exothermic decomposition of the solute was essential for the preparation of nanometre particles by spray pyrolysis. Therefore, the nature of disintegration of the FEAG process is different from the heat-driven explosion that plays a major role in the previous work [4].

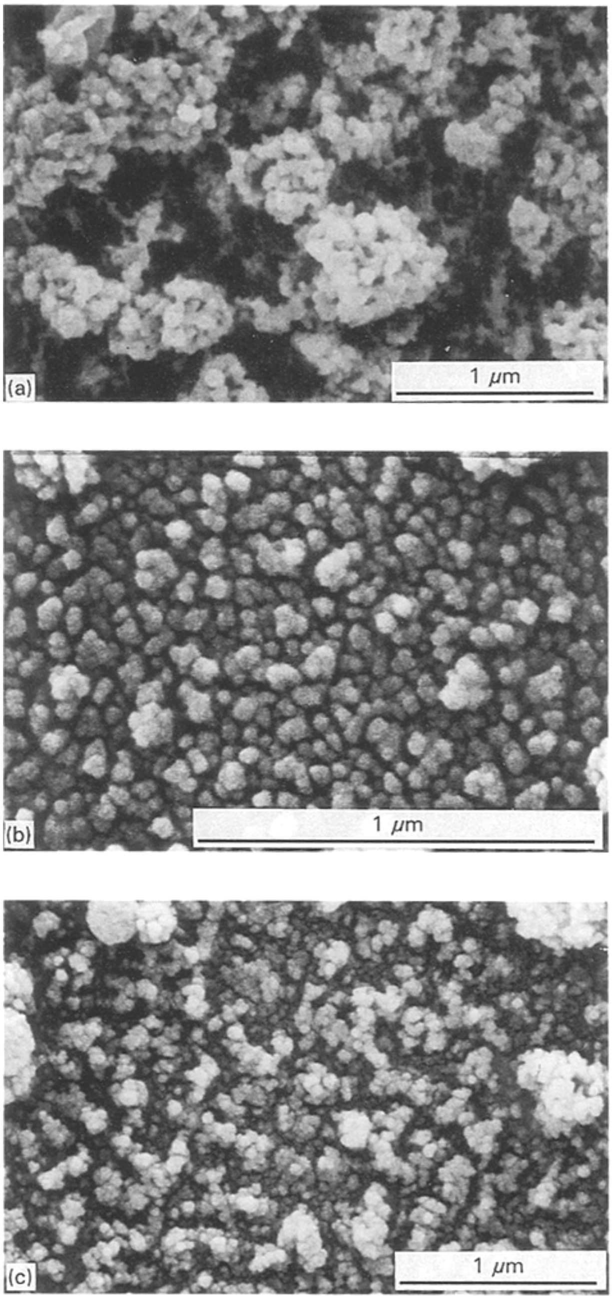

Figure 11 SEM photographs of various oxide particles prepared by the FEAG process (0.75 M Mn acetate, 0.2 M Pd nitrate, 0.1 M Cu nitrate, 600 °C, 60 torr).

3.4. Other nanometre particles formation in FEAG process

Fig. 11 shows the SEM photographs of various oxide particles prepared from Mn acetate, Pd nitrate and Cu nitrate solutions by the FEAG process. Sproson and Messing [4] reported that the nitrate salts decomposed to form oxides by a series of endothermic reactions while the acetates decomposed with exothermic reactions. In these cases, disintegration of dried primary particles occurred not only from acetate salts, which decomposed exothermically, but also from nitrate salts which decomposed endothermically. Sproson and Messing [4] showed that disintegration of primary particles did not occur at higher temperature (1000 °C) from manganese acetate solution, whereas disintegration occurred and nanometre particles were formed by the FEAG process at low temperature (600 °C).

Therefore, we conclude that nanometre oxide particles can be prepared from various acetate and nitrate solutions by disintegration of dried primary particles. Especially, several tens of nanometre particles without carbon contamination can be prepared from various nitrate solutions at low temperature by the FEAG process.

4. Conclusions

A filter expansion aerosol generator (FEAG), which produced an aerosol stream of 2 μm droplets at the liquid flow rate of 5 ml min^{-1}, was applied to the generation of nanometre particles by spray pyrolysis.

Zinc oxide particles smaller than 20 nm were produced from zinc acetate solution by the FEAG process. The shape of these particles were distinctively different from the one produced by the ultrasonic spray pyrolysis process from the drying stage. XRD and TGA results showed that 0.02 s residence time was long enough to produce crystalline zinc oxide particles of 3 wt % weight loss at 600 °C.

The FEAG process was also used for producing 60 nm silver particles from silver nitrate solution, which was decomposed endothermically. The formation mechanism was also the same as the formation of zinc oxide particles. Therefore, exothermic decomposition of the solute is not a necessary condition for the disintegration of the primary particles in the FEAG process. This result opened up an opportunity for producing carbon-free nanometre particles from nitrate solutes.

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