

# Preparation of High Surface Area $\text{MgAl}_2\text{O}_4$ Particles from Colloidal Solution using Filter Expansion Aerosol Generator

Yun Chan Kang, Jeong Su Choi and Seung Bin Park\*

Department of Chemical Engineering, Korea Advanced Institute of Science & Technology, 373-1 Kusong-dong Yusong-gu, Taejeon 305-701, Korea

(Received 6 January 1997; accepted 26 September 1997)

## Abstract

Magnesium aluminate particles with high surface area were directly prepared from colloidal solutions by spray pyrolysis using a filter expansion aerosol generator. The colloidal solution was prepared by hydrolysis of aluminum isopropoxide (AIP) and magnesium salts. The spinel particles began to form from 900°C. When prepared from colloidal solutions, the particles have porous and hollow morphology in contrast to particles prepared from aqueous solutions which have solid morphology. In the colloidal solution, the mean size of the spinel particles measured from the SEM photographs was increased from 0.42 to 0.95  $\mu\text{m}$  when the overall solution concentration was increased from 0.075 to 0.1  $\text{mol l}^{-1}$ . The specific surface areas of particles prepared from colloidal solutions were 264 and 259  $\text{m}^2 \text{g}^{-1}$  when acetate and nitrate was used as magnesium source, respectively. On the other hand, particles prepared from aqueous solutions had low surface areas (18 and 23  $\text{m}^2 \text{g}^{-1}$ ) when acetate and nitrate were used as magnesium source, respectively. © 1998 Elsevier Science Limited. All rights reserved

## 1 Introduction

Magnesium aluminate is used as catalyst, sensor and component in various electronic devices.<sup>1–3</sup> Fine particles with high surface area are required for high reactivity and selectivity. These characteristics are also required for highly sinterable particles.

Solid state reaction,<sup>4</sup> chemical coprecipitation,<sup>2,5,6</sup> and spray pyrolysis<sup>3,7</sup> have been used for the production of magnesium aluminate spinel. In

solid state reaction, high reactor temperature (> 1400°C) and long heating time are required for phase pure spinel particles. Therefore, spinel particles prepared by solid state reaction have large size and low surface area. Coprecipitation method also requires a long heating time, even if the sintering temperature is lower than powders prepared by solid state reaction.

Spray pyrolysis is a continuous process different from the above two processes. Particles prepared by spray pyrolysis have high surface areas due to the short residence times of the particles inside the high temperature zone. In spite of this short residence time, single phase, multicomponent particles are formed due to the high reactivity of submicron size particles with stoichiometric composition. Suyama and Kato prepared magnesium aluminate spinel particles from mixed aqueous solutions by spray pyrolysis using a pneumatic nozzle.<sup>3</sup> They showed that spinel particles prepared by spray pyrolysis had a high surface area (50–100  $\text{m}^2 \text{g}^{-1}$ ) and the form of hollow spheres. Kanzaki *et al.* reported that the specific surface area and the pore volume of magnesium aluminate spinel particles prepared by spray pyrolysis depended on the type of solvent.<sup>7</sup> The specific surface areas of particles varied from 22 to 109  $\text{m}^2 \text{g}^{-1}$  depending on the type of solvent.

Recently, colloidal solutions obtained from the hydrolysis of alkoxide precursors have been used to prepare high surface area particles by spray pyrolysis. Messing *et al.* reported that nanocomposite particles of  $\gamma\text{-Al}_2\text{O}_3$  and platinum prepared by spray pyrolysis from a hybrid sol of  $\text{H}_2\text{PtCl}_6$  dissolved in a boehmite sol had surface area as high of 203  $\text{m}^2 \text{g}^{-1}$ .<sup>8</sup> Kang *et al.*<sup>9</sup> reported that lithium aluminate particles prepared by ultrasonic spray pyrolysis from aqueous solution of aluminum nitrate and lithium formate had lower

\*To whom correspondence should be addressed.

surface area ( $7 \text{ m}^2 \text{ g}^{-1}$ ) than particles ( $45 \text{ m}^2 \text{ g}^{-1}$ ) prepared from a colloidal solution obtained from aluminum isopropoxide and lithium formate.

In this study, magnesium aluminate spinel particles were prepared from colloidal and aqueous solutions by spray pyrolysis using a filter expansion aerosol generator. The influence of the type of solution on the crystallinity and morphology of the particles was investigated. The spinel particles prepared from colloidal solution had larger surface area ( $264 \text{ m}^2 \text{ g}^{-2}$ ) than that ( $18 \text{ m}^2 \text{ g}^{-1}$ ) of particles prepared from aqueous solution.

## 2 Experimental

The apparatus used in this work was a filter expansion aerosol generator (FEAG), of which details have appeared elsewhere.<sup>10,11</sup> In the FEAG process, the solutions are atomized into droplets of  $2 \mu\text{m}$  at  $5 \text{ ml min}^{-1}$  and delivered into a hot-wall reactor at 60 torr. As the aerosol stream passes through the reactor, the solvent evaporates and the metal salts decompose into individual oxide particles. The reaction of individual particles into single phase multicomponent oxide particles then follows in the high temperature of the reactor.

The starting solutions were prepared using two different methods. The colloidal solution was prepared from aluminum isopropoxide and magnesium salts. Aluminum isopropoxide (AIP) was hydrolyzed at  $85^\circ\text{C}$  to form the aluminum hydroxide sol. Peptization then formed a clear sol. This peptized sol was composed of fibrils with lengths of several tens of nanometres. Stoichiometric amounts of magnesium salt were dissolved in this clear sol.

The aqueous solution was prepared from aluminum nitrate and magnesium acetate or nitrate. The stoichiometric amounts of aluminum and magnesium salt were dissolved in distilled water.

The overall concentration of aluminum and magnesium source was changed from  $0.0075$  to  $0.15 \text{ mol l}^{-1}$ . Air was used as carrier gas. The reactor temperature was maintained isothermally at between  $800$  to  $1000^\circ\text{C}$ . The residence time of the particles in the hot wall reactor was varied between  $0.01$  to  $0.02 \text{ s}$  depending on the reactor temperature.

The prepared particles were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and multi-point BET analysis.

## 3 Results and Discussion

The XRD spectra of particles prepared from colloidal and aqueous solutions are shown in Figs 1–4.

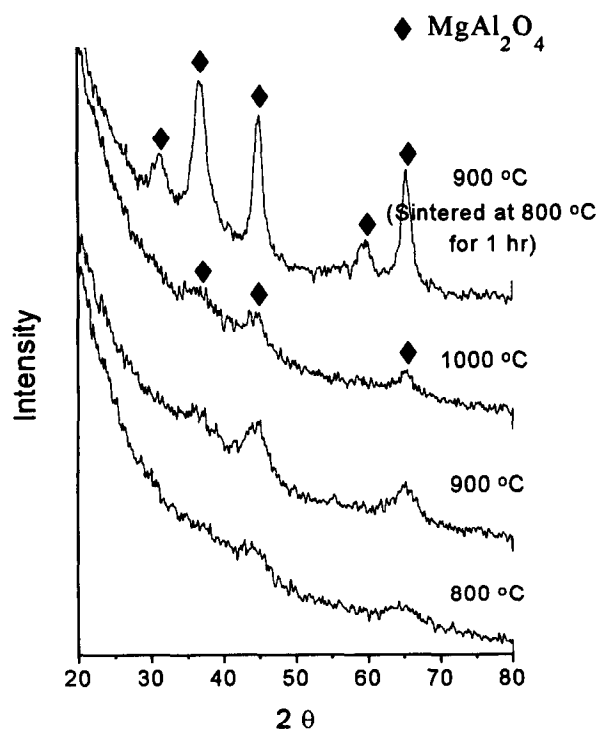


Fig. 1. XRD spectra of particles prepared from colloidal solution obtained from aluminum isopropoxide and magnesium acetate.

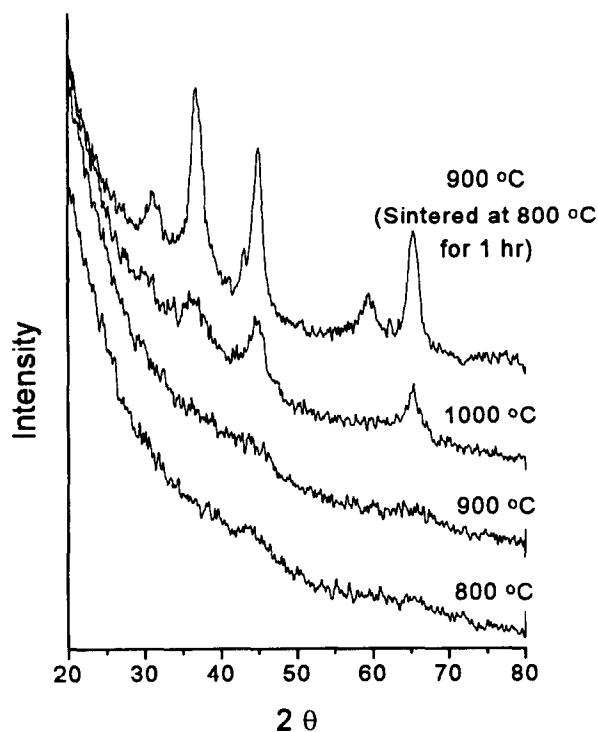


Fig. 2. XRD spectra of particles prepared from colloidal solutions obtained from aluminum isopropoxide and magnesium nitrate.

The spinel particles began to form from  $900^\circ\text{C}$  regardless of the type of aluminum and magnesium source. The spinel particles are poorly crystallized due to the short residence times in the FEAG process, while the particles calcined at  $800^\circ\text{C}$  for 1 h have high crystallinity. The calcined particles were

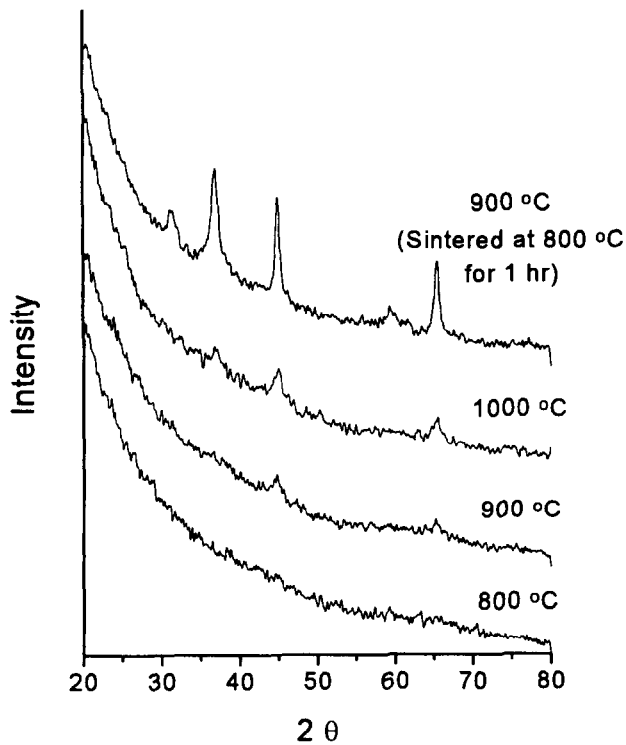


Fig. 3. XRD spectra of particles prepared from aqueous solution obtained from aluminum nitrate and magnesium acetate.

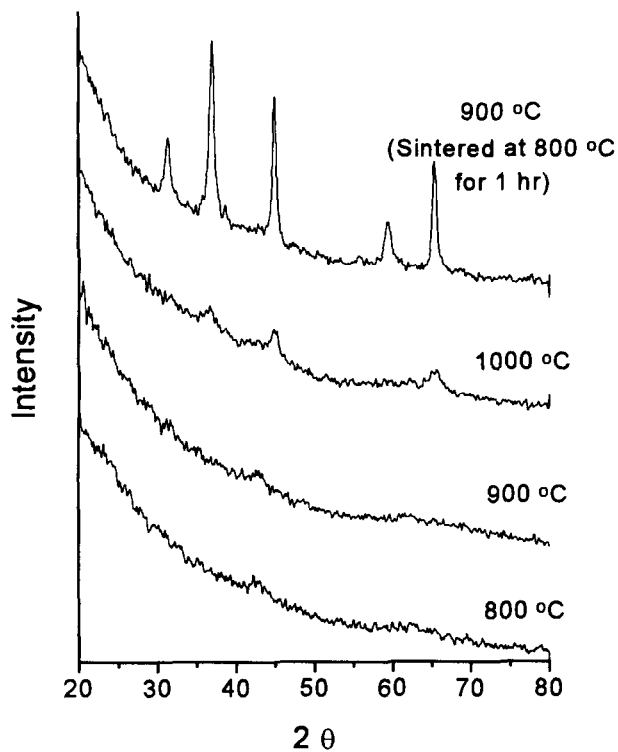
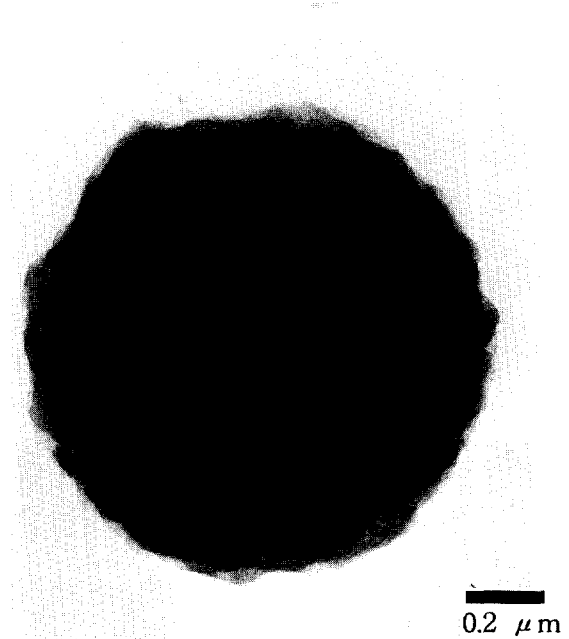


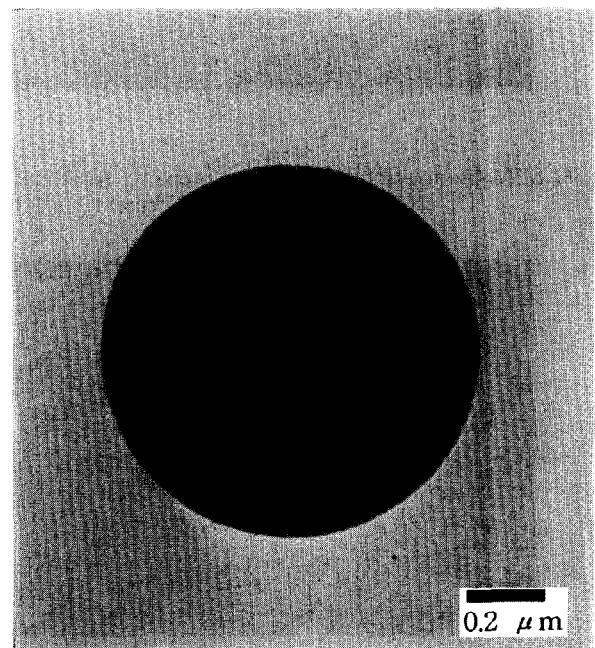
Fig. 4. XRD spectra of particles prepared from aqueous solution obtained from aluminum nitrate and magnesium nitrate.

not agglomerated, and the mean size of the particles was not changed by the above calcining conditions from the evidence of SEM photographs.

Figure 5 shows TEM photographs of particles prepared from colloidal and aqueous solutions.



(a) AIP + Mg acetate



(b) Al nitrate + Mg acetate

Fig. 5. TEM photographs of particles prepared from colloidal and aqueous solution.

Magnesium acetate was used as magnesium source. The overall solution concentration and reactor temperature were  $0.15 \text{ mol l}^{-1}$  and  $900^\circ\text{C}$ , respectively. The particles prepared from aqueous solution have a completely smooth surface and dense morphology, while the particles prepared from colloidal solution have rough surface and porous morphology. The morphology of spinel particles was not affected by the type of magnesium salts.

Figures 6 and 7 show SEM photographs of spinel particles prepared at different concentrations from colloidal and aqueous solutions, respectively.

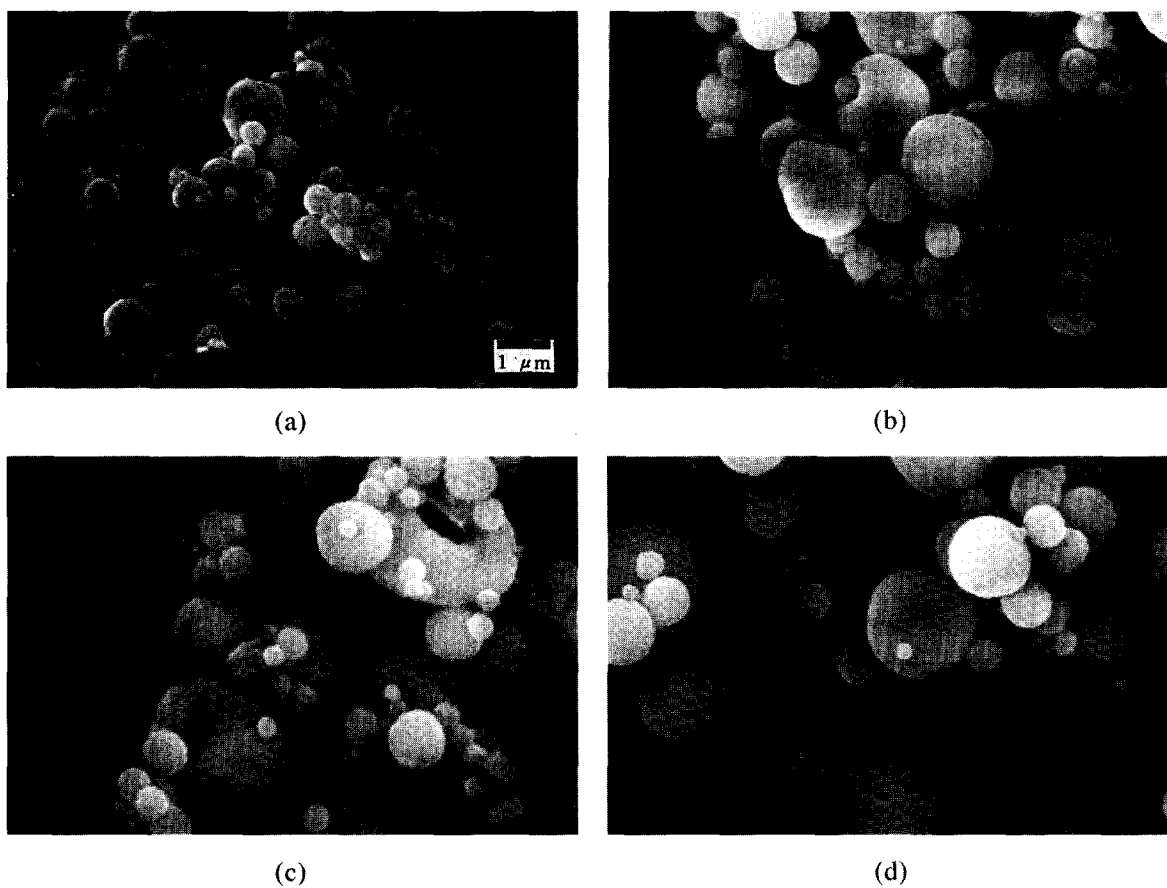


Fig. 6. SEM photographs of particles prepared from colloidal solution obtained from aluminum isopropoxide and magnesium acetate: (a)  $0.0075 \text{ mol l}^{-1}$ ; (b)  $0.03 \text{ mol l}^{-1}$ ; (c)  $0.06 \text{ mol l}^{-1}$ ; (d)  $0.1 \text{ mol l}^{-1}$ .

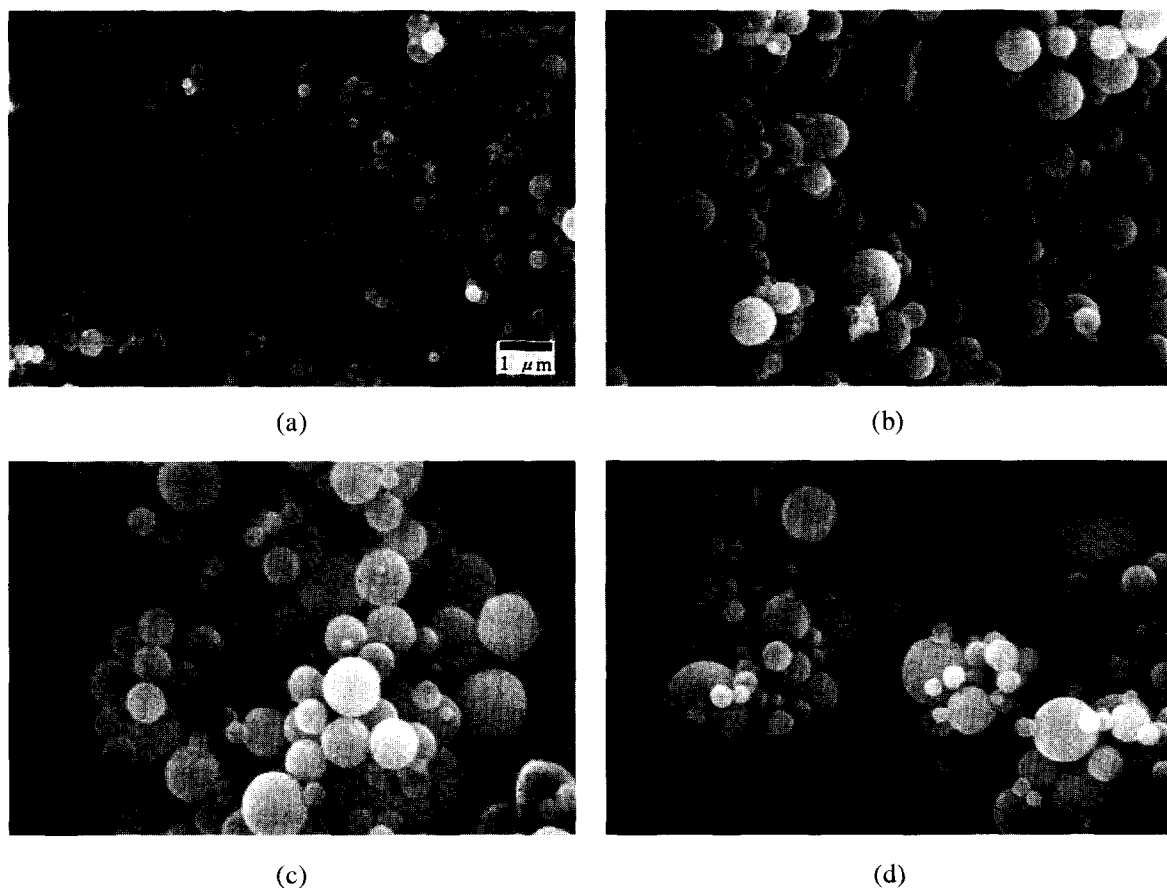


Fig. 7. SEM photographs of particles prepared from aqueous solution obtained from aluminum nitrate and magnesium acetate: (a)  $0.0075 \text{ mol l}^{-1}$ ; (b)  $0.03 \text{ mol l}^{-1}$ ; (c)  $0.06 \text{ mol l}^{-1}$ ; (d)  $0.1 \text{ mol l}^{-1}$ .

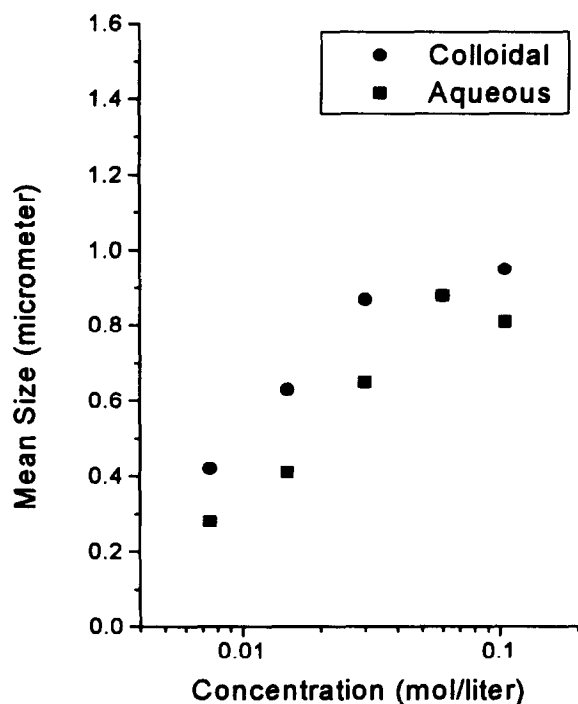


Fig. 8. Mean sizes of spinel particles measured from the SEM photographs.

In Fig. 6, the particles prepared from colloidal solution had hollow shape, and holes formed from the gas evolution were observed in some particles. In Fig. 7, a small fraction of the spherical particles prepared from aqueous solution was fractured into two parts, and holes were not observed. From these fractured particles, it is observed that the insides of the particles are filled with small primary particles. Figure 8 shows the mean sizes of particles measured from the SEM photographs. Magnesium acetate was used as magnesium source, and the reactor temperature was fixed at  $900^{\circ}\text{C}$ . The spinel particles prepared from colloidal solutions have larger size than particles prepared from aqueous solutions on the evidence of the SEM photographs. In the colloidal solution, the mean size of the spinel particles measured from the SEM photographs was increased from 0.42 to 0.95  $\mu\text{m}$  when the overall solution concentration was increased from 0.0075 to 0.1  $\text{mol l}^{-1}$ .

The specific surface area of the spinel particles was strongly affected by the type of solution. The overall concentration of solution was maintained at 0.15  $\text{mol l}^{-1}$  for the measurement of the specific surface area of particles. The reactor temperature was fixed at  $900^{\circ}\text{C}$ . The specific surface areas of particles prepared from colloidal solutions were 264 and 259  $\text{m}^2 \text{g}^{-1}$  when acetate and nitrate was used as magnesium source, respectively. On the other hand, the particles prepared from aqueous solutions had low surface areas (18 and 23  $\text{m}^2 \text{g}^{-1}$ ) when acetate and nitrate was used as magnesium source, respectively. These differences of surface

area in colloidal and aqueous solutions are due to the difference in precipitation mechanism. In the case of colloidal solution, precipitation of magnesium salt could rapidly occur by heterogeneous precipitation on the fibrils of aluminum hydroxides. On the other hand, dense particles were formed at the drying stage by homogeneous precipitation in the absence of nuclei in the case of the aqueous solutions. When the particles prepared from colloidal solution were calcined at  $800^{\circ}\text{C}$  for 1 h, the specific surface area of the particles was reduced from 264  $\text{m}^2 \text{g}^{-1}$  to 124  $\text{m}^2 \text{g}^{-1}$  due to the crystallite growth of particles. Such high surface area spinel particles are attractive for catalysts and sensors.

#### 4 Conclusions

Magnesium aluminate particles were prepared from colloidal and aqueous solutions by spray pyrolysis. The crystallinity of particles was not affected by the type of aluminum and magnesium source. The particles prepared directly from colloidal and aqueous solutions had poor crystallinity of spinel due to the short residence times in the FEAG process, while particles calcined at  $800^{\circ}\text{C}$  for 1 h had good crystallinity. The spinel particles prepared from colloidal solution had spherical and hollow shape, while the particles prepared from aqueous solution had solid morphology. The particles prepared from colloidal solutions had larger surface areas than those of aqueous solutions due to the high nucleus concentration precipitation in the colloidal solutions.

#### References

- Muraki, H. and Fujitani, Y., Steam reforming of n-heptane using a  $\text{Rh/MgAl}_2\text{O}_4$  catalyst, I. Support and kinetics. *Appl. Catal.*, 1989, **47**, 75–84.
- Gusmano, G., Nunziante, P., Traversa, E. and Chiozzini, G., The mechanism of  $\text{MgAl}_2\text{O}_4$  spinel formation from the thermal decomposition of coprecipitated hydroxides. *J. Europ. Ceram. Soc.*, 1991, **7**, 31–39.
- Suyama, Y. and Kato, A., Characterization and sintering of Mg–Al spinel prepared by spray-pyrolysis technique. *Ceramurgia Inter.*, 1992, **8**(1), 17–21.
- Bakker, W. T. and Lindsay, J. G., Reactive magnesia spinel, Preparation and properties. *Am. Ceram. Soc. Bull.*, 1967, **46**(7), 649–652.
- Bratton, R. J., Coprecipitates yielding  $\text{MgAl}_2\text{O}_4$  spinel powders. *Am. Ceram. Soc. Bull.*, 1969, **48**(8), 759–762.
- Bratton, R. J., Characterization and sintering of reactive  $\text{MgAl}_2\text{O}_4$  spinel. *Am. Ceram. Soc. Bull.*, 1969, **48**(11), 1069–1075.
- Kanzaki, S., Hirao, K., Otsuka, N., Saito, K., Nakagawa, Z. and Hamano, K., Characterization of spray pyrolysis spinel powders. *Yugio-Kyokai-Shi*, 1983, **91**(2), 81–86.
- Messing, G. L., Chang, S. C. and Jayanthi, G. V., Ceramic powder synthesis by spray pyrolysis. *J. Am. Ceram. Soc.*, 1993, **76**(11), 2707–2726.

9. Kang, Y. C., Park, S. B. and Kwon, S. W., Preparation of submicron size lithium aluminate particles from the mixture of alumina sol and lithium salt by ultrasonic spray pyrolysis. *J. Colloid and Inter. Sci.*, 1996, **182**, 59–62.
10. Kang, Y. C. and Park, S. B., A high-volume spray aerosol generator producing small droplets for low pressure applications. *J. Aerosol Sci.*, 1995, **26**(7), 1131–1138.
11. Kang, Y. C. and Park, S. B., Preparation of nanometer size oxide particles using filter expansion aerosol generator. *J. Mater. Sci.*, 1996, **31**, 2409–2416.