

Nano-sized MgO particles ranging from 13 to 28 nm synthesized by spray pyrolysis

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Nano-sized MgO particles with well-crystallized structures were prepared by spray pyrolysis from spray solutions with citric acid. The optimum concentration of citric acid to prepare micrometre-sized MgO precursor particles in the spray pyrolysis was 0.4 M. The addition of citric acid to the spray solution affected the thermal properties and morphologies of the precursor particles. The micrometre-sized precursor particles with hollow and porous structures obtained by spray pyrolysis turned to nano-sized MgO particles after post-treatment. The post-treated MgO particles had aggregation-free nanometre sizes after simple milling by hand using an agate mortar. The mean sizes of the MgO particles measured from high magnification TEM photographs at post-treatment temperatures of 500 and 900°C were 13 and 28 nm. The addition of citric acid to the spray solutions decreased the mean sizes of the primary particles at the same post-treatment temperatures. The mean crystallite sizes of the post-treated particles obtained from the spray solution with citric acid at post-treatment temperatures of 500 and 900°C were 9 and 22 nm.

Key words: spray pyrolysis, nano particle, magnesium oxide.

Introduction

Magnesium oxide (MgO) is one of the most important metal oxides, which has great potential for use in a wide range of applications due to its predominant thermal, optical, electrical and chemical properties [1-4]. The nano-sized MgO particles can be used as the filling subjects in painting, paper, cosmetics, plastic, rubber, and as the co-assistant materials of some electric materials [5]. In addition, MgO films have also been developed as protective layers for dielectrics to improve the discharge characteristics and the panel's lifetime in plasma display panels (PDP) due to their refractory property and their secondary electron emission coefficient [6, 7]. In the PDP industries, MgO protective layers are mainly formed by an e-beam process operating under high vacuum conditions. Therefore, the formation process of a MgO protective layer is an obstacle to the cost reduction for PDP. A MgO protecting layer should be formed using nano-sized MgO particles to reduce the PDP production costs [8].

There are several processes reported in the literature for the synthesis of nano-sized MgO particles. Bhargava et al. synthesized nano-sized MgO particles from magnesite ore by a wet chemical method [9]. Duan et al. prepared MgO nano particles with an average size of 30 nm by a sol-gel method using magnesium chloride and a NaOH aqueous solution as the raw materials [10]. However, post-treatment at high temperatures are necessary to

obtain the MgO particles with high crystallinity and no impurities such as a carbon component. However, a post-treatment process performed to improve the characteristics of the particles causes a size growth and aggregation between the particles.

The spray pyrolysis process has been successfully applied to synthesize submicrometre-sized ceramic particles with narrow size distributions, uniform shapes, and controlled purities [11-13]. Recently, polymeric precursors were introduced to prepare nano-sized ceramic particles by spray pyrolysis [14-16]. The precursor particles obtained by spray pyrolysis from the polymeric precursor solution had hollow and porous morphologies. The precursor particles with hollow and porous morphologies turned to nano-sized ceramic particles after post-treatment at high temperatures.

In this study, nano-sized MgO particles were prepared by spray pyrolysis. The micrometre-sized precursor particles obtained by spray pyrolysis from the spray solution with citric acid turned to nano-sized MgO particles with narrow size distributions after a post-treatment. The effects of the concentrations of citric acid added to the spray solution and the post-treatment temperature of the precursor particles on the formation of nano-sized MgO particles were investigated.

Experimental procedure

The precursor particles were prepared by ultrasonic spray pyrolysis from spray solutions with and without citric acid. A schematic diagram of the spray pyrolysis system used in this work is cited elsewhere [17]. The system consisted of a droplet generator, a quartz reactor and a particle collector. A 1.7-MHz ultrasonic spray

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generator with six vibrators was used to generate droplets, which were then carried into the high-temperature tubular reactor by a carrier gas. The length and diameter of the quartz reactor were 1200 and 50 mm, respectively. The flow rate of air used as the carrier gas was fixed at 45 l minute⁻¹. The high flow rate of the carrier gas was applied to improve the hollow and porous structures of the precursor particles by increasing the drying and decomposition rates of droplets and particles. The temperature of the reactor was fixed at 900°C. The residence time of the particles inside the hot wall tubular reactor was 0.6 s. To prepare the spray solution, magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in distilled water. The overall solution concentration of magnesium nitrate hexahydrate was 0.2 M. The concentration of citric acid used as a polymeric precursor was changed from 0 to 0.8 M. The precursor particles obtained by spray pyrolysis were post-treated in a box furnace at temperatures between 500 and 900°C.

The crystal structures of the precursor and post-treated MgO particles were investigated using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The mean crystallite sizes of the MgO particles were calculated using Scherrer's equation. The thermal properties of the precursor MgO particles were measured using a thermo-analyzer (TG-DSC, Netzsch, STA409C, Germany) in the temperature

range from 40 to 900°C. The morphological characteristics of the MgO particles were investigated using scanning electron microscopy (SEM, JEOL, JSM-6060) and high resolution transmission electron microscope (TEM, FEI, TECHNAI 300K).

Results and discussion

The key idea in this study to prepare the nano-sized MgO particles with high crystallinity and no impurities after post-treatment at high temperatures is to make precursor particles with hollow and porous structures. The morphologies of the precursor MgO particles obtained from the spray solutions with and without citric acid are shown in Fig. 1. The precursor particles obtained from the spray solution without citric acid had a size of several micrometres and a filled structure, whereas the precursor particles obtained from the spray solution with citric acid had hollow and thin walled structures. The addition of citric acid to the spray solution increased the mean sizes of the precursor particles. In addition, the hollowness of the precursor particles was affected by the concentrations of citric acid added to the spray solutions. The optimum concentration of citric acid to prepare the MgO precursor particles with thin walls and hollow structures was 0.4 M. The high drying and decomposition rates of particles and the gas evolution

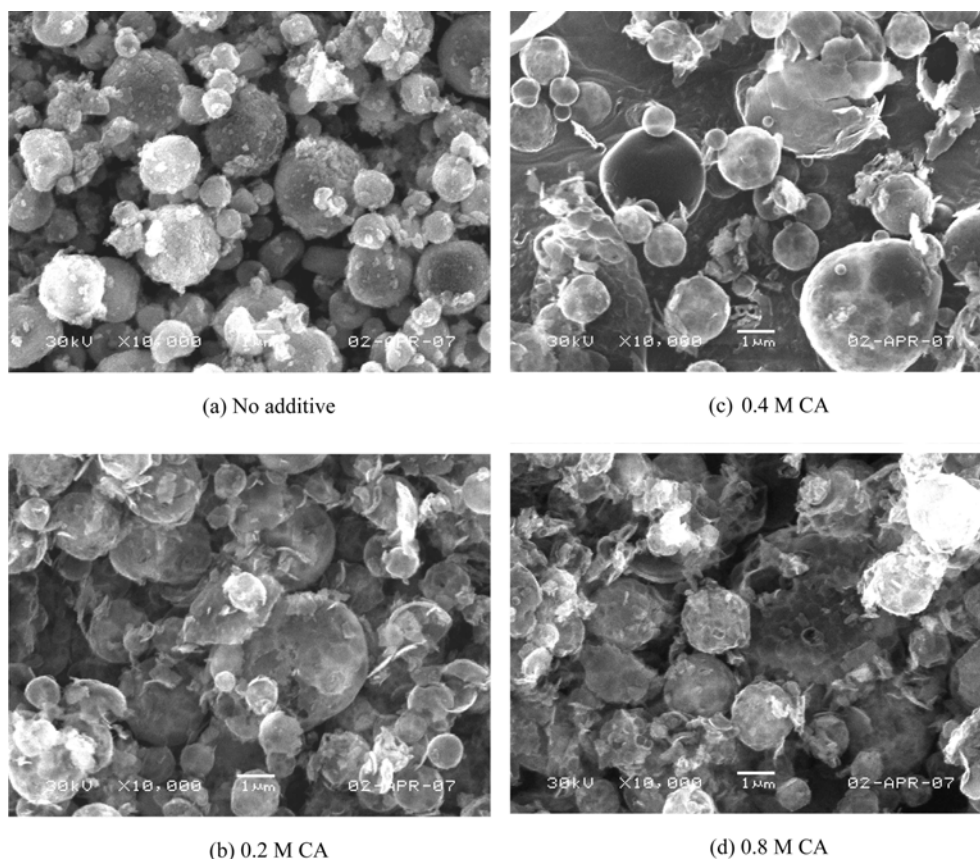


Fig. 1. SEM photographs of as-prepared MgO particles obtained by spray pyrolysis.

from the decomposition of the citric acid generated the precursor particles with hollow and thin walled structures. However, the precursor particles obtained by spray pyrolysis from the spray solution with citric acid had impurities such as a carbon component because of the short residence time of the particles inside the hot wall tubular reactor. Therefore, post-treatment of the precursor particles at high temperatures is required to remove the impurities such as the carbon components.

The thermal analyses of the MgO precursor particles obtained by spray pyrolysis from the spray solutions with and without citric acid are shown in Fig. 2. The concentration of citric acid was 0.4 M. The TG curves of the precursor particles clearly show that there are two weight losses at temperatures below 900°C. The first pronounced weight loss at temperatures below 200°C is related to the evaporation of water molecules adsorbed on the precursor particles obtained from the spray solutions with and without citric acid. Correspondingly, endothermic peaks are observed in the DSC curves at temperatures below 200°C. However, the second weight losses were different in the precursor particles obtained from the spray solutions with and without citric acid. The addition of citric acid to the spray solution changed the types of DSC curve of the precursor particles. The

DSC curve of the precursor particles obtained from the spray solution without citric acid showed an endothermic peak with high intensity at 330°C. The endothermic peak at 330°C was due to the decomposition of $\text{Mg}(\text{NO}_3)_2$. On the other hand, an endothermic peak at 330°C in the DSC curve of the precursor particles obtained from the spray solution with citric acid was not observed. The complete decomposition of the $\text{Mg}(\text{NO}_3)_2$ occurred in the spray pyrolysis process using the spray solution with citric acid. The heat evolved from the decomposition of citric acid inside the particles increased the temperature of the precursor particles. Therefore, complete decomposition of the $\text{Mg}(\text{NO}_3)_2$ occurred with the preparation condition of a short residence time of the particles inside the hot wall tubular reactor. The exothermic peak of the precursor particles obtained from the spray solution with citric acid at 430°C appeared by decomposition of the carbon component contained inside the precursor particles. Therefore, the weight losses in the TG curves of the precursor particles obtained from the spray solutions with and without citric acid occurred by different mechanism.

Fig. 3 gives micrographs of the precursor particles obtained by spray pyrolysis which were post-treated at a temperature of 900°C for 2 h. The spherical shape of the precursor particles was maintained after post-treatment at a high temperature. However, the inner structures of the post-treated MgO particles were affected by the concentrations of citric acid added to the spray solutions. The MgO particles prepared from the spray solution without citric acid had a filled inner structure and aggregated morphology of the primary particles with a nanometre size. On the other hand, the MgO particles prepared from the spray solutions with citric acid had hollow and porous structures. The degree of aggregation of the primary particles with nanometre sizes was affected by the concentration of citric acid added to the spray solutions. The MgO particles obtained from the spray solution with the optimum concentration of citric acid as 0.4 M had a slightly aggregated morphology of nanometre-sized primary particles. A high concentration of citric acid added to the spray solution increased the degree of aggregation of the primary particles. Fig. 4 shows SEM photographs of the MgO particles milled by hand using an agate mortar. After this simple milling process, the post-treated MgO particles obtained from the spray solution without citric acid had a bimodal particle size distribution of nanometre and micrometre size particles. The post-treated MgO particles with a filled inner structure and hardly an aggregated morphology were not crushed to the nanometre-sized particles by the simple milling process. Micrometre-sized particles were observed in the sample obtained from the spray solution with a low concentration of citric acid at 0.2 M. On the other hand, the MgO particles obtained from the spray solutions with high concentrations of citric acid above 0.4 M had nanometre sizes after the simple milling process.

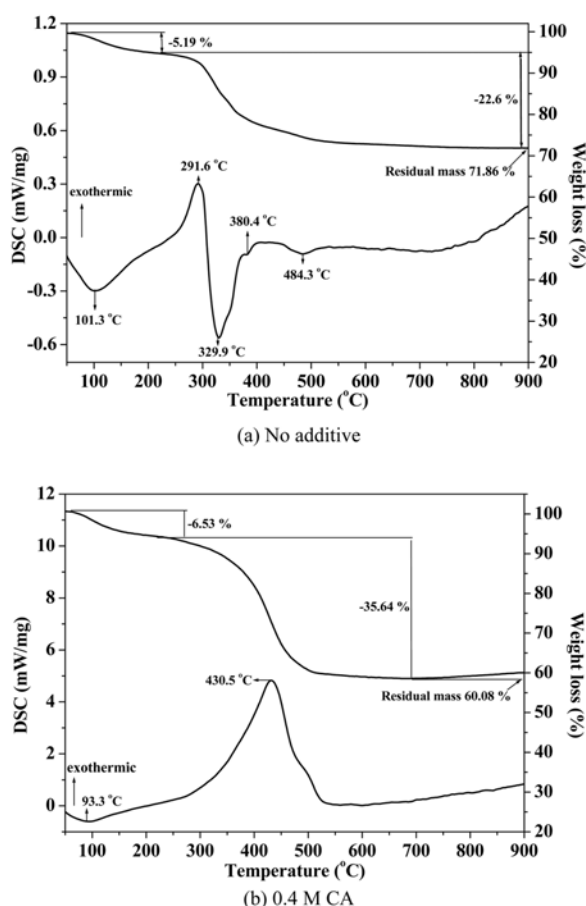


Fig. 2. TG/DSC curves of as-prepared MgO particles obtained by spray pyrolysis

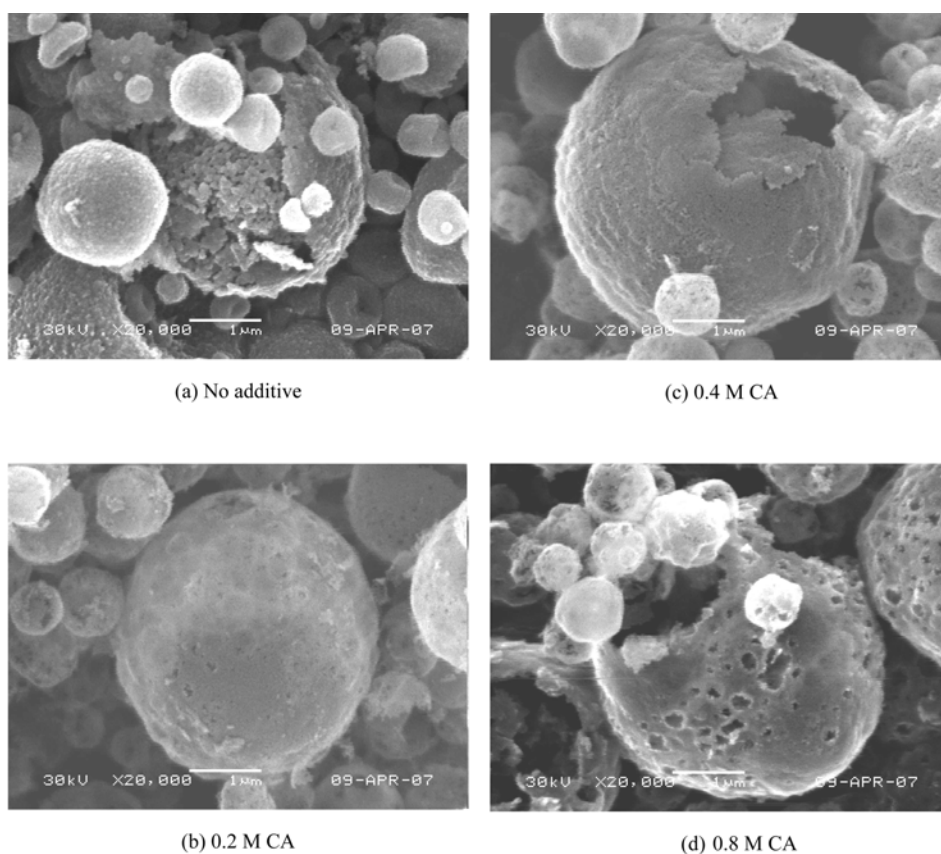


Fig. 3. SEM photographs of MgO particles post-treated at temperature of 900°C

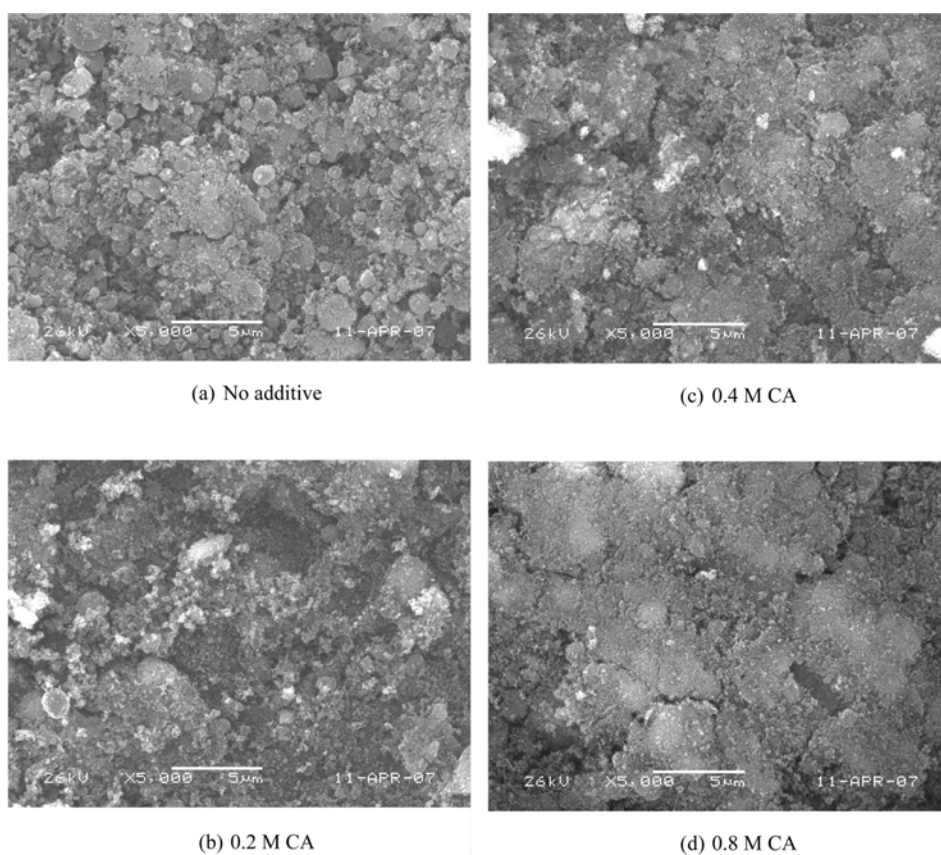
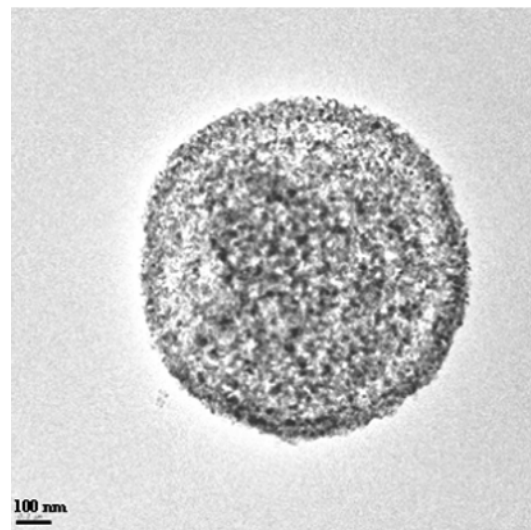


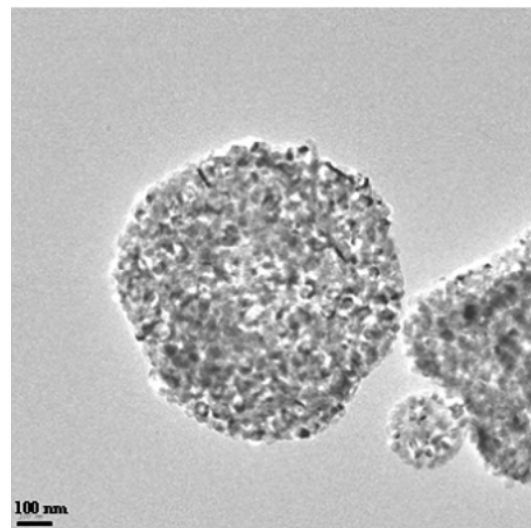
Fig. 4. SEM photographs of post-treated MgO particles after a simple milling process.

The mean sizes and morphologies of the primary particles comprising the post-treated MgO particles obtained from the spray solutions with and without citric acid were investigated in high magnification TEM photographs. Fig. 5 shows TEM photographs of the MgO particles prepared from the spray solution without citric acid at post-treatment temperatures of 500 and 900°C. The post-treated MgO particles had a spherical shape and micrometre size of the aggregated primary particles with a nanometre size. The mean sizes of the primary particles measured from the high magnification TEM photographs were 19 and 33 nm at post-treatment temperatures of 500 and 900°C respectively. Fig. 6 shows the TEM photographs of the MgO particles obtained from the spray solution with the concentration of citric acid at 0.4 M. The mean sizes of the primary particles measured from the high magnification TEM photographs at post-treatment temperatures of 500 and 900°C were each 13 and 28 nm. The addition of citric acid to the spray solutions decreased the mean sizes of the primary particles at the same post-treatment temperatures. The thin wall structure and high porosity of the precursor particles obtained from the spray solutions with citric acid decreased the mean sizes of the primary particles.

The XRD patterns of the post-treated MgO particles obtained from spray solutions with and without citric acid are shown in Fig. 7. The concentration of citric acid added to the spray solution was 0.4 M. The post-treated particles had a pure MgO phase at post-treatment temperatures of 500 and 900°C irrespective of the types of spray solution. However, the crystallinities of the MgO particles were affected by the type of the spray solution. The mean crystallite sizes of the MgO particles were calculated from Scherrer's equation. The mean crystallite sizes of the post-treated particles obtained from the spray solution without citric acid at post-treatment temperatures of 500 and 900°C were 15 and 24 nm. On the other hand, the mean crystallite sizes of the post-treated particles obtained from the spray solution with citric acid at post-treatment temperatures

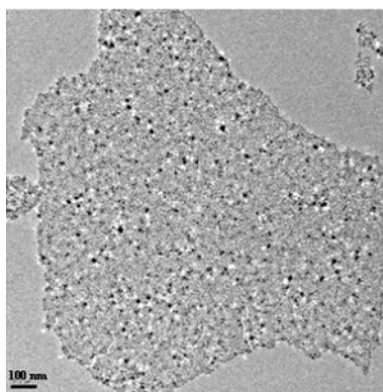


(a) A 500

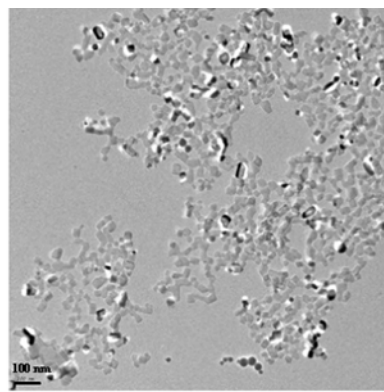


(b) A 900

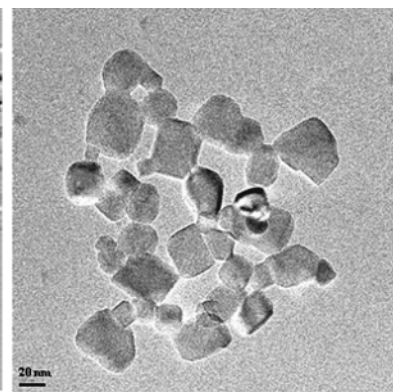
Fig. 5. TEM photographs of MgO particles obtained from the spray solutions without citric acid.



(a) A 500



(b) A 900



(c) A 900

Fig. 6. TEM photographs of MgO particles obtained from the spray solutions with 0.4M citric acid.

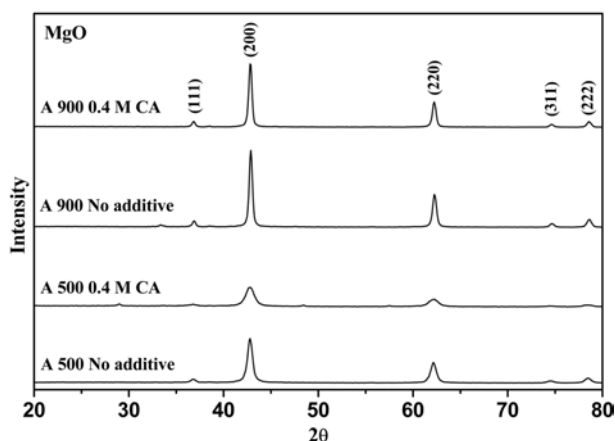


Fig. 7. XRD spectra of MgO particles prepared from the spray solutions with and without citric acid.

of 500 and 900°C were 9 and 22 nm. The results from the XRD spectra of the post-treated MgO particles coincided well with those from the TEM photographs as shown in Figs. 5 and 6. That is, the MgO particles obtained from the spray solutions with citric acid had finer crystallite and mean sizes than those obtained from the spray solution without citric acid.

Conclusions

In this study, in the spray pyrolysis, nano-sized magnesium oxide particles were prepared at high post-treatment temperatures. The high post-treatment temperatures formed the nano-sized MgO particles with high crystallinity and no impurities. The degree of aggregation of the MgO particles decreased after post-treatment at high temperatures. The mean sizes and crystallite sizes of the nano-sized MgO particles obtained by spray pyrolysis were changed in varying the concentrations of citric acid added to the spray solutions and the post-treatment temperatures.

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