SYNTHESIS OF MAGNESIUM ALUMINATE SPINEL NANOPARTICLES BY CO-PRECIPITATION METHOD: THE INFLUENCES OF PRECIPITANTS

Karn Serivalsatit[1,2,*], Sarut Teerasoradech[1,2], and Adison Saelee[1,2]

Received: August 22, 2012; Revised: December 25, 2012; Accepted: January 8, 2013

Abstract

Magnesium Aluminate Spinel ($MgAl_2O_4$) nanoparticles were synthesized by the co-precipitation method using 2 different precipitants, i.e., urea and ammonium bicarbonate. The precipitated precursor synthesized using urea as a precipitant was a platelet-like hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\bullet 4H_2O$). The hydrotalcite decomposed to MgO and an amorphous phase after calcining at 600°C for 2 h. The formation of $MgAl_2O_4$ via a reaction between MgO and the amorphous phase was observed after calcining over 800°C for 2 h, while the precipitated precursor synthesized using ammonium bicarbonate as a precipitant was an unidentified low crystalline phase. The precipitated precursor decomposed to an amorphous phase after calcining at 600°C for 2 h. MgA_2O_4 was obtained after calcining over 800°C for 2 h. In addition, after calcining at 1100°C for 2 h, the equiaxed $MgAl_2O_4$ nanoparticles with a particle size in the range of 10 to 30 nm were obtained from both methods. However, the $MgAl_2O_4$ nanoparticles synthesized using ammonium bicarbonate as a precipitant exhibited a higher specific surface area (74.61 m2/g).

Keywords: $MgAl_2O_4$, co-precipitation, nanoparticles, urea, ammonium bicarbonate

Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) is widely used in many applications, such as refractories (Ghosh *et al.*, 2004) , transparent armours (Grujicic *et al.*, 2012), infrared transmitting devices (Krell *et al.*, 2010), and high pressure lamp envelopes (Wei, 2009), because of its high melting point, high mechanical strength, high resistance to chemical attack, and excellent optical and dielectric properties. $MgAl_2O_4$ powder is conventionally prepared by calcining the mixture of magnesia and alumina at a temperature over 1600°C, followed by ball milling to obtain fine powders (Ryskhewitch, 1960). However, it is difficult to obtain fine and reactive $MgAl_2O_4$ powders by the

---

[1] *Research Unit of Advanced Ceramics, Deartment of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand. E-mail: karn.s@chula.ac.th*

[2] *Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand*

[*] *Corresponding author*

conventional method because a high reaction temperature leads to the grain growth and hard agglomeration of $MgAl_2O_4$ particles, which is undesirable for the fabrication of dense $MgAl_2O_4$ ceramics.

In order to obtain high purity, nano-sized, and non-agglomerated particles, various chemical techniques, such as sol-gel (Varnier *et al.*, 1994), solution precipitation (Li *et al.*, 2001), spray pyrolysis (Bickmore *et al.*, 1996; Suyama and Kato, 1982), and combustion synthesis (Bhaduri *et al.*, 1999), have been developed. Among the above-mentioned methods, co-precipitation using organic salts has been verified for its feasibility for the fabrication of $MgAl_2O_4$ nanoparticles with narrow size distribution and low agglomeration. Moreover, it is relatively convenient and cost-effective.

In this present work, $MgAl_2O_4$ nanoparticles were synthesized by co-precipitation method using 2 different precipitants, namely ammonium bicarbonate (NH_4HCO_3) and urea ($CO(NH_2)_2$). The effects of the precipitants on morphology and nanoparticles characteristics as well as phase evolution during calcination were investigated.

Materials and Methods

Aluminium nitrate nanohydrate ($Al(NO_3)3\bullet 9H_2O$, AR Grade, QReC, Pulau Pinang, Malaysia) and magnesium nitrate hexahydrate ($Mg(NO_3)3\bullet 6H_2O$, 98%, Panreac Quimica Sau, Barcelona, Spain) were used as starting materials. The mixture of aluminium and magnesium nitrate solution was prepared by dissolving aluminium nitrate nanohydrate and magnesium nitrate hexahydrate at the spinel stoichiometry of a 2:1 ratio in distilled water. The concentration of the nitrate solution was 0.3 M for Mg^{2+} and 0.15 M for Al^{3+}. For using ammonium bicarbonate as a precipitant, 20 ml of 1.5 M ammonium bicarbonate solution was prepared by dissolving ammonium bicarbonate (98%, Ajax Finechem, Auckland, New Zealand) in distilled water. The spinel precursor was prepared by adding 80 ml of the mixed salts solution into the ammonium bicarbonate solution under mild stirring at room temperature. The resultant suspension was centrifuged after being stirred for another hour. The precipitated precursor was washed with distilled water several times and then dried at 100°C overnight. For using urea as a precipitant, 36.036 g of urea (99.5%, Acros Organics, Morris Plains, NJ, USA) was added into 200 ml of the mixed salt solution. The solution was stirred under mild stirring at 85°C for 24 h. The precipitated precursor was separated from the suspension by centrifugation. Finally, the precursor was washed with distilled water several times and then dried at 100°C overnight.

The morphology of the precursors and nanoparticles was observed using scanning electron microscopy (SEM, JEM-64000 LV, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2100, JEOL, Tokyo, Japan). Phase evolution of the precursor during calcination was investigated using X-ray diffractometry (XRD, D8, Bruker, Karlsruhe, Germany) and Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet 6700, Thermo Scientific, Southend-on-Sea, UK). The crystallite size was estimated from the Scherrer equation.

$$D_{XRD} = \frac{0.94\,\lambda}{\beta cos\theta}$$

where D_{XRD} is the average crystallite size; λ is the X-ray wavelength (0.15404 nm), and θ and β are the diffraction angle and FWHM of the peak, respectively. The specific surface area of the $MgAl_2O_4$ nanoparticles was measured by the Brunauer-Emmett-Teller (BET) method on a surface area analyzer (SA-3100, Coulter, Brea, CA, USA). The equivalent particle size (D_{BET}) could be estimated from the specific surface area using

$$D_{BET} = \frac{6}{\rho \bullet S}$$

where ρ is the theoretical density of $MgAl_2O_4$, which is 3.58 g/cm^3 and S is the specific surface area of the $MgAl_2O_4$ nanoparticles

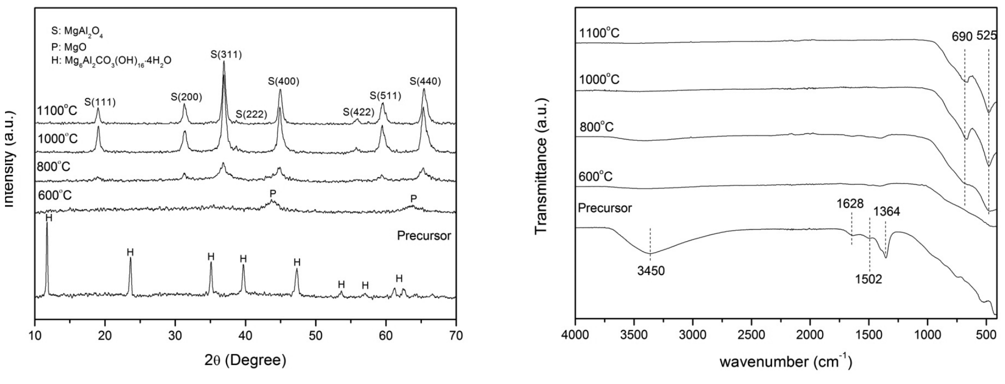
Results and Discussion

XRD patterns of the precipitated precursor prepared using urea as a precipitant and its calcined products at various temperatures are shown in Figure 1(a). The XRD pattern of the precipitate precursor shows diffraction peaks characteristic of hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}{\bullet}4H_2O$; JCPDS card no. 89-0460). After calcining at 600°C for 2 h, the hydrotalcite decomposed to periclase (MgO; JCPDS card no.45-0946) and the amorphous phase, which could be amorphous alumina (Wajler *et al.*, 2008). The formation of MgAl2O4 (JCPDS card no. 21-1152) is observed after calcining at 800°C for 2 h via the solid state reaction between MgO and the amorphous phase. Further increasing the calcining temperature leads to the enhancement of diffraction peak intensities and also the reduction of the full-width at half-maximum of the peaks due to the improvement of crystallinity and its grain growth.

Figure 1(b) shows FT-IR spectra of the precipitated precursor prepared using urea as a precipitant and its calcined products at various temperatures. The precipitated precursor exhibits the broad absorption band of OH centered around 3450 cm^{-1}, and the absorption band of H_2O vibration at 1628 cm^{-1} (Guo *et al.*, 2004). The broad absorption peaks centered at 1502 cm^{-1} and 1364 cm^{-1} are characteristics of CO_3^{2-} vibration (Das *et al.*, 2003). The presence of the absorption peaks of OH, H_2O, and CO_3^{2-} corresponds to the phase identification from the XRD result. However, the intensity of these absorption peaks decreases after calcining at 600°C for 2 h, indicating the decomposition of the hydrotalcite.

The precursors calcined above 800°C show double peaks centered at 690 and 525 cm^{-1}. These peaks are attributable to the vibration of AlO_6, which built up $MgAl_2O_4$ (Guo *et al.*, 2004).

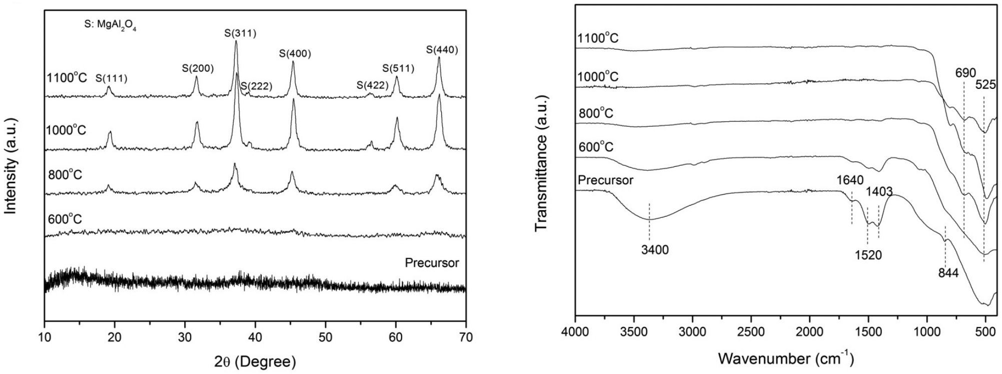
Figure 2(a) shows XRD patterns of the precipitated precursor prepared using ammonium bicarbonate as a precipitant and its calcined products at various temperatures. The XRD pattern of the precipitate precursor shows the broad peaks, indicating low crystallinity, which cannot be assigned to any known phase. The low crytalline phase decomposes to the amorphous phase after calcining at 600°C for 2 h. Peaks corresponding to $MgAl_2O_4$ begin to appear in the XRD pattern of the powder calcined at 800°C for 2 h. Further increasing the calcining temperature improves the crystallinity of $MgAl_2O_4$, as confirmed by the change in the full-width at half-maximum and the intensity of the peaks.



(a) **(b)**

Figure 1. (a) XRD patterns and (b) FT-IR spectra of of the precipitated precursor prepared using urea as a precipitant and its calcined products at various temperatures for 2 h

The FT-IR spectra of the precipitated precursor prepared using ammonium bicarbonate as a precipitant and its calcined products at various temperatures are shown in Figure 2(b). The precipitated precursor also exhibits the absorption of a hydrate carbonate compound. The absorption peaks centered at 3400 and 1640 cm^{-1} are characteristics of OH and H_2O vibration, respectively. The characteristic absorption bands of the CO_3^{2-} can be observed at 1520, 1403, and 844 cm^{-1} (Li *et al.*, 2000). The differences in shape and position of the absorption peaks, compared to those of the precursor prepared using urea, could be due to the different crystal structure. These absorption peaks disappear after calcining at 800°C,



(a) (b)

Figure 2. (a) XRD patterns and (b) FT-IR spectra of the precipitated precursor prepared using ammonium bicarbonate as a precipitant and its calcined products at various temperatures for 2 h

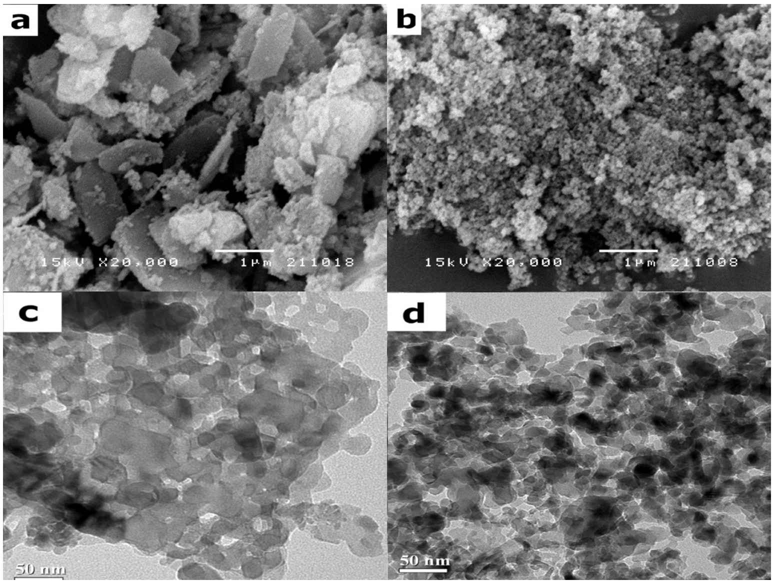


Figure 3. (a and b) SEM micrographs of the precursor prepared using urea and ammonium bicarbonate, respectively and (c and d) TEM images of the calcined nanopowders at 1100°C for 2 h, prepared using urea and ammonium bicarbonate, respectively

while the vibration of AlO_6 at 690 and 525 cm^{-1} appears, indicating the formation of $MgAl_2O_4$.

The morphology of the precursors prepared using urea and ammonium bicarbonate and their calcined powders at 1100°C for 2 h are compared in Figure 3(a)-(d). The precursor prepared using urea shows a platelet-like structure, which is a typical morphology of the hydrotalcite (Figure 3(a)). The size of the platelet-like hydrotalcite is in the range of 1-10 micron. Some sub-micron particles are observed due to a direct result of mechanical crushing. After calcining at 1100°C for 2 h, the platelet-like structure decomposes to individual $MgAl_2O_4$ nanoparticles with the particle size of 10-30 nm, as shown in Figure 3(c). The morphology of the precursor prepared using ammonium bicarbonate is shown in Figure 3(b). The precursor is equiaxed and assembles to form the agglomerates. The precursor converts to $MgAl_2O_4$ nanoparticles with the particle size of 10-30 nm after calcining at 1100°C for 2 h, as shown in Figure 3(d).

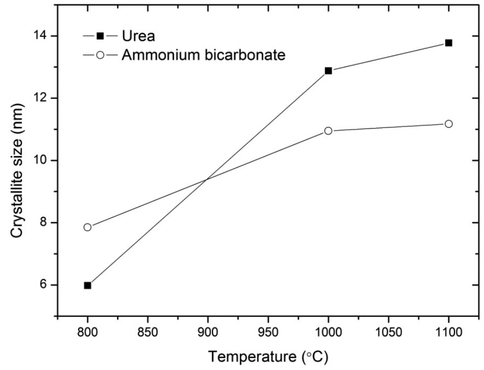


Figure 4. Crystallite size of $MgAl_2O_4$ nanopowders calcined at various temperatures

The crystallite size (D_{XRD}) and the specific surface area of the calcined powders were also investigated in order to compare the reactivity of both nanopowders. The estimated crystallite size was calculated using the Scherrer equation. The crytallite size of the powders calcined at 800-1100°C for 2 h is shown in Figure 4. For the use of urea as a precipitant, the crystallite size increases from 6 to 13 nm, when the calcination temperature increases from 800 to 1100°C, while the crystallite size of the calcined powders, prepared using ammonium bicarbonate as a precipitant, increases from 7 to 11 nm. The crystallite sizes of both nanopowders are almost identical. The crystallite size of the nanopowders increases markedly as the calcination temperature increases, indicating particle growth during calcination. The specific surface area, the equivalent particle size (D_{BET}), and the crystallite size (D_{XRD}) of the nanopowders calcined at 1100°C for 2 h are summarized in Table 1. Even the crystallite sizes estimated using the Scherrer equation of both nanopowders are almost identical; the specific surface area of the nanopowder, parepared using ammonium bicarbanate, is higher than that of the nanopowder, prepared using urea. In addition, D_{BET} of both nanopowders are larger than D_{XRD}, indicating an agglomeration of nanopowders. However, the nanopowder prepared using ammonium bicarbonate exhibits a lower degree of agglomeration.

Table 1. The specific surface area, the equivalent particle size (D_{BET}), and the crystallite size (D_{XRD}) of the nanopowders calcined at 1100°C for 2 h

Precipitant	Specific surface area (m^2/g)	Equivalent particle size (D_{BET}) (nm)	Crystallite size (D_{XRD}) (nm)
Urea	47.24	35	13
Ammonium bicarbonate	74.61	22	11

Conclusions

Synthesis of $MgAl_2O_4$ nanoparticles by co-precipitation using urea and ammonium bicarbonate as a precipitant was investigated. The study of phase evolution during calcination and microstructure observation revealed that the precipitants affect the phase evolution and agglomeration degree of the prepared nanopowders significantly. The use of urea as a precipitant produces a platelet-like hydrotalcite, while the use of ammonium bicarbonate produces an unidentified low-crystalline phase. However, both precursors convert to $MgAl_2O_4$ after calcining at 800°C for 2 h. Although the crystallite sizes of both $MgAl_2O_4$ nanopowders are similar, the surface area of the nanopowder prepared using ammonium bicarbonate is higher than that of the nanopowder prepared using urea, which is favorable for the fabrication of $MgAl_2O_4$ ceramics.

Acknowledgments

This work has been supported by Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University and partly by the Defence Science and Technology Department, Ministry of Defence and the National Electronics and Computer Technology Center.

References

Bhaduri, S., Bhaduri, S.B., and Prisbrey, K.A. (1999). Auto ignition synthesis of nanocrystalline $MgAl_2O_4$ and related nanocomposites. J. Mater. Res., 14(9):3571-3580.

Bickmore, C.R., Waldner, K.F., Treadwell, D.R., and Laine, R.M. (1996). Ultrafine spinel powders by flame spray pyrolysis of a magnesium aluminum double alkoxide. J. Am. Ceram. Soc., 79 (5):1419-1423.

Das, D.P., Das, J., and Parida, K. (2003). Physico-chemical characterization and adsorption behavior of calcined Zn/Al hydrotalcite-like compound (HTlc) towards removal of fluoride from aqueous solution. J. Colloid Interf. Sci., 261(2):213-220.

Ghosh, A., Sarkar, R., Mukherjee, B., and Das, S.K. (2004). Effect of spinel content on the properties of magnesia-spinel composite refractory. J. Eur. Ceram. Soc., 24(7):2079-2085.

Grujicic, M., Bell, W.C., and Pandurangan, B. (2012). Design and material selection guidelines and strategies for transparent armor systems. Mater. Design, 34:808-819.

Guo, J.J., Lou, H., Zhao, H., Wang, X.G., and Zheng, X.M. (2004). Novel synthesis of high surface area $MgAl_2O_4$ spinel as catalyst support. Mater. Lett., 58(12-13):1920-1923.

Krell, A., Hutzler, T., Klimke, J., and Potthoff, A. (2010). Fine-grained transparent spinel windows by the processing of different nanopowders. J. Am. Ceram. Soc., 93(9):2656-2666.

Li, J.-G., Ikegami, T., Lee, J.-H., and Mori, T. (2000). Characterization of yttrium aluminate garnet precursors synthesized via precipitation using ammonium bicarbonate as the precipitant. J. Mater. Res., 15(11):2375-2386.

Li, J. G., Ikegami, T., Lee, J.H., Mori, T., and Yajima, Y. (2001). A wet-chemical process yielding reactive magnesium aluminate spinel ($MgAl_2O_4$) powder. Ceram. Int., 27(4):481-489.

Ryskhewitch, E. (1960). Oxide Ceramics. Academic Press, NY, 271p.

Suyama, Y. and Kato, A. (1982). Characterization and sintering of Mg-Al spinel prepared by spray-pyrolysis technique. Ceram. Int., 8(1):17-21.

Varnier, O., Hovnanian, N., Larbot, A., Bergez, P., Cot, L., and Charpin, J. (1994). Sol-gel synthesis of magnesium aluminum spinel from a heterometallic alkoxide. Mater. Res. Bull., 29(5):479-488.

Wajler, A., Tomaszewski, H., Drozdz-Ciesla, E., Weglarz, H., and Kaszkur, Z. (2008). Study of magnesium aluminate spinel formation from carbonate precursors. J. Eur. Ceram. Soc., 28(13):2495-2500.

Wei, G.C. (2009). Transparent ceramics for lighting. J. Eur. Ceram. Soc., 29(2):237-244.