J Mater Sci (2009) 44:2992–2998
DOI 10.1007/s10853-009-3397-8

LETTER

A novel approach for synthesis of nanocrystalline $MgAl_2O_4$ powders by co-precipitation method

M. M. Rashad · Z. I. Zaki · H. El-Shall

Received: 23 October 2008 / Accepted: 16 March 2009 / Published online: 2 April 2009

Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) posseses a unique combination of desirable properties such as high melting point (2,135 °C), good mechanical strength at room and evaluated temperatures, high chemical inertness, low dielectric constant and electrical losses, good shock resistance, and excellent optical properties [1]. Due to these desirable properties, it has a wide range of applications in structural, chemical, optical, and electrical industries. $MgAl_2O_4$ has mainly been used as refractory in heavy industry and as substrate for solid-state electronic devices. Nowadays, new potential applications have been reported including; ceramic ultra-filtration membranes, electro-insulators, and optical materials such as optically transparent, fiber-optic temperature sensors, tunable solid-state lasers, matrix for fabrication of optical nanodevices, high-brightness phosphor screen, catalysis, and humidity sensor applications. Furthermore, the $MgAl_2O_4$ spinel has been employed as excellent transparent ceramic materials for high temperature arc-enclosing envelopes and alkali-metal vapor discharge devices [2–9].

Thus, it is important to obtain the spinel of high purity using an easy preparation method. The solid-state synthesis of $MgAl_2O_4$ spinel, as conventional synthesis technique, requires higher temperature and longer reaction time so that the synthesized powder suffers from agglomeration and low sinter activity. Thus, the preparation of magnesium aluminate powders with high purity, chemical homogeneity, control of stoichiometry, fine particle size, narrow particle size distribution, and minimum particle agglomeration with high sinter activity has received considerable attention in order to improve the material properties [10]. Numerous wet chemical methods have been employed to synthesize magnesium aluminate fine particles including sol–gel [11, 12], co-precipitation [13–15], hydrothermal [16, 17], microwave-assisted combustion processing [18], microemulsion [19], metal-organic processing [20–23], spray drying [24], freeze drying [25], and mechanochemical synthesis [26, 27] techniques. The chemical co-precipitation method [28–31] ensures proper distribution of various metals ions resulting into stoichiometric and smaller particle sized product compared to some of the others. Moreover, the process is a low-cost technique suitable for the mass production compared to the other mentioned methods. The main drawback is that the particle size is not small and monodispersed enough for specific applications.

To the best of our knowledge, no published study in the literature on synthesis of $MgAl_2O_4$ has so far used the co-precipitation method with organic reagents. Most publications about organic precursor technique, which involves the preparation of aqueous solution, required cation, the chelation of cations in solution by addition of carboxylic acid then, raising the temperature of the solution until formation of the precursor. The precursor is calcined at low temperature compared with other methods to form the powder, where the quasi-atomic dispersion of constituent components in liquid precursors facilitates synthesis of the crystallized powder.

M. M. Rashad (✉) · Z. I. Zaki
Central Metallurgical Research and Development Institute,
P.O. Box 87, Helwan, Cairo, Egypt
e-mail: rashad133@yahoo.com

H. El-Shall
Engineering Research Center, Materials Science
and Engineering, University of Florida, Gainesville,
FL 32611, USA

The method is also called combustion method, polymeric precursor method, acids gel method (oxalate precursor, tartaric acid, lactic acid, etc.), and also Pechini-type process (Citrate precursor method). The organic precursor was not only used to form stable complexes with starting metallic ions but also used as organic rich fuel [20–23]. This study aims to synthezise the spinel magnesium aluminate nanopowders using 8-hydroxyquinoline (HQ) and tetraethyl ammonium hydroxide (TEAOH). The changes in phase formation, crystallite size, density, specific surface area, particle size distribution, and powder morphology were systematically studied.

Experimental

Materials and processing

All the chemicals and reagents used were of high purity. The materials used were anhydrous aluminum chloride $AlCl_3$, anhydrous magnesium chloride $MgCl_2$, TEAOH $(C_2H_5)_4NOH$, and 8-HQ C_9H_7NOH.

For the co-precipitation using TEAOH, the chloride salts of aluminum and magnesium ions at molar ratio 2:1 were dissolved in 100 mL bi-distilled water with magnetic stirring. The solution was precipitated at pH 11 using TEAOH. After 15 min, the precipitate was filtered off and washed with deionized water. Then, the produced precursor was dried at 100 °C overnight. The formed precursors (white solids) were heated again to 600, 800, and 1,000 °C at a rate of 10 °C/min and kept at the these temperatures for 2 h.

The chemical reactions for synthesis of magnesium aluminate nanopowders can be expressed as follows [32]:

$$2AlCl_3 + MgCl_2 + 5(C_2H_5)_4NOH \rightarrow 2Al(OH)_3 \cdot Mg(OH)_2 + 5(C_2H_5)_4NCl$$

$$2Al(OH)_3 \cdot Mg(OH)_2 \xrightarrow{heat} MgAl_2O_4 + 4H_2O$$

The remaining tetraethyl ammonium chloride was converted into carbon dioxide, water, nitric oxide, and hydrogen chloride.

To process magnesium aluminate spinel powders using 8-hydroxyquinoline (HQ), a stoichiometric amount of anhydrous magnesium chloride $MgCl_2$ and anhydrous aluminum chloride $AlCl_3$ at Mg^{2+}:Al^{3+} mole ratio 1:2 was dissolved in deinoized water at room temperature using hot plate magnetic stirrer. The desired volume of 8-HQ dissolved in acetone was added to the solution until pH 7 [32]. Yellow precipitate is formed instantaneously. The precipitate was evaporated at 80 °C and then dried at 200 °C for 2 h. The dry precursors formed were heated (annealed) at a rate of 10 °C/min in static air atmosphere up to different temperatures (600–1,000 °C) where they were maintained for 2 h.

The reactions of HQ with magnesium and aluminum were as follows [32]:

$$MgCl_2 + 2AlCl_3 + 5C_9H_7NOH \rightarrow Mg(C_9H_7NO)_2 \cdot 2Al(C_9H_7NO)_3 + 5HCl$$

$$Mg(C_9H_7NO)_2 \cdot 2Al(C_9H_7NO)_3 + 85O_2 \xrightarrow{heat} MgAl_2O_4 + 72CO_2 + 18H_2O + 8NO_2$$

Physical techniques

XRD patterns of the resulting products were characterized by a Brucker D8-advance X-ray powder diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). The crystallite sizes of the produced magnesium aluminate for the most intense peak plane: (311) for HQ and (440) for TEAOH estimated from the X-ray diffraction data using the Debye–Scherrer formula:

$$d_{RX} = k\lambda/\beta\cos\theta$$

where d_{RX} is the crystallite size, $k = 0.9$ is a correction factor to account for particle shapes, β is the full width at half maximum (FWHM) of the most intense diffraction peak (311) plane, λ is the wavelength of Cu target = 1.5406 Å, and θ is the Bragg angle.

The bulk density of the fired powders was evaluated using Archimedes method. S_{BET} specific surface areas were recorded using Quantachrome Nova 1200 series. The changes in crystal morphologies of the $MgAl_2O_4$ particles produced at elevated temperature of 1,000 °C for different processing routes were examined by scanning electron microscopy (JEOL-JSM 5410 SEM). For analysis of particle size distribution, a laser diffraction particle size analysis method using Coulter LS 13 320 was performed. The particle size distribution (number or volume percent) of the suspension synthesized using certain weight of the powder sample in 10 mL water, then ultrasonic to avoid the agglomeration of the powder. The data of the particles size distribution in the water solution were obtained by the computer-controlled coulter LS 13 320 instrument via a software program.

Results and discussion

XRD diffraction patterns for the produced magnesium aluminate spinel powders synthesized by co-precipitation method using TEAOH and HQ (8-HQ) routes at different

Fig. 1 XRD patterns of the formed $MgAl_2O_4$ powders annealed at 600–1,000 °C for 2 h precipitated using tetraethyl ammonium hydroxide (TEAOH)

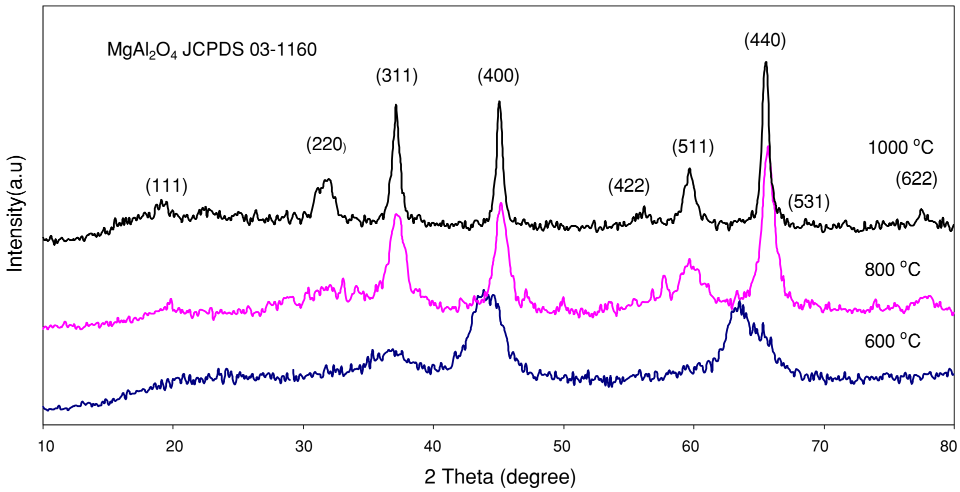
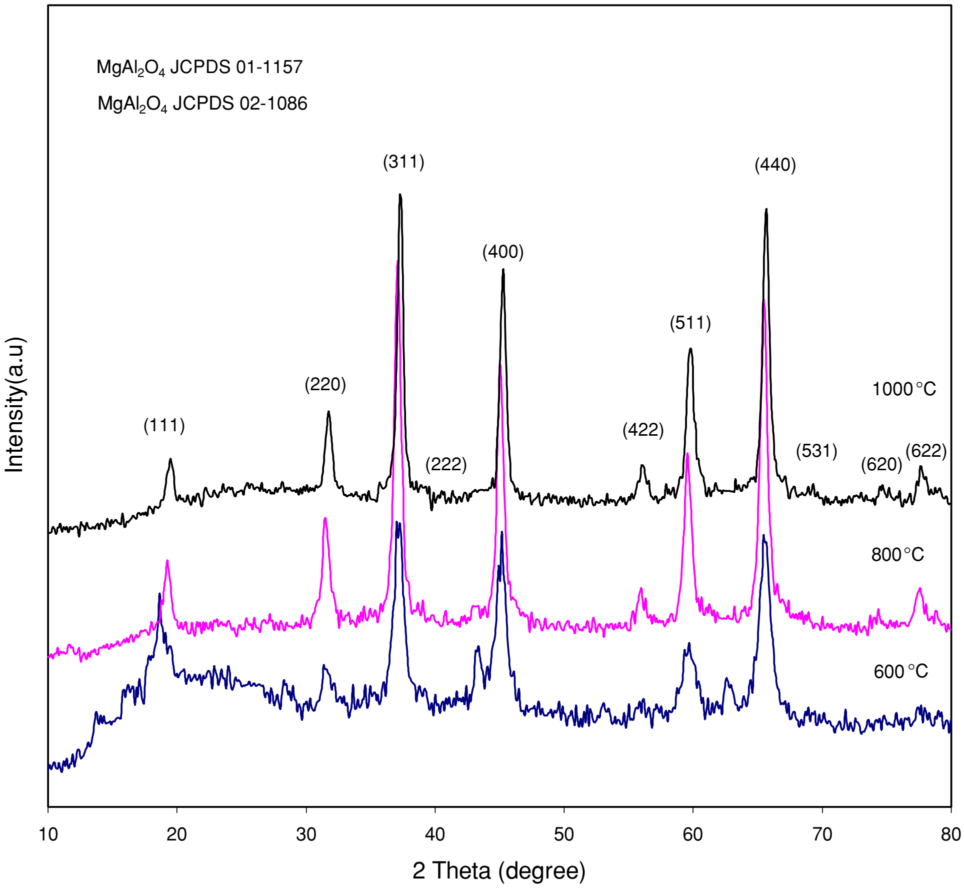


Fig. 2 XRD patterns of $MgAl_2O_4$ powders annealed from 600 to 1,000 °C for 2 h using 8-hydroxyquinoline (HQ) as a precipitation agent



annealing temperatures 600–1,000 °C for 2 h are shown in Figs. 1 and 2. For the produced magnesium aluminate spinel from precursor with TEAOH annealed at temperature 600 °C, XRD patterns showed broad XRD peaks with a very fine crystallite size (8.3 nm). After annealing the precursor at 800 °C, a single phase of well-formed crystalline spinel cubic $MgAl_2O_4$ phase (JCPDS card # 03-1160) was found. The strongest three peaks of the produced powders appeared at 2θ values of 65.52°, 44.98°, and 37.13°. These peaks corresponded to (440), (400), and (311) diffraction planes of $MgAl_2O_4$ phase which is characterized from the patterns as face-centered cubic, space group: Fd3 m, lattice parameter (a) 8.045, Z(coordination number) 8 and melting point 2,135 °C. At high annealing temperature 1,000 °C, a well-formed crystalline magnesium aluminate spinel phase was obtained.

Table 1 Crystallite size (CS) of the produced $MgAl_2O_4$ prepared at different annealing temperatures ranging from 600 to 1,000 °C using TEAOH and HQ as precipitating compounds

Temperature, °C	Crystallite size (CS), nm	
	With TEAOH	With HQ
600	8.30	25.30
800	25.72	31.78
1,000	32.42	33.17

$MgAl_2O_4$ crystallite size, (311) plane was considered for crystallite size calculation in case of HQ $MgAl_2O_4$ crystallite size, (440) plane was considered for crystallite size calculation in case of TEAOH

This means a gradual increase in crystallite size as a function of increasing heat-treatment temperature. The crystallite size of the single-phase $MgAl_2O_4$ powders formed was calculated from XRD analyses using Debye–Scherrer formula of the most intense peak (440) which was increased by increasing the annealing temperature. Table 1 illustrates the increase in the crystallite sizes of the magnesium aluimate spinel powders formed by increasing the annealing temperatures. The crystallite size increased from 8.3 nm at 600 °C to 25.72 nm at 800 °C, and then increased to 32.42 nm by increasing the annealing temperature to 1,000 °C.

Figure 2 showed the XRD patterns of the produced magnesium aluminate powders at different annealed temperatures using HQ to form the precipitated precursors. It can be observed that spinel magnesium aluminate powders (JCPDS card # 02-1086 or 01-1157) were obtained at low annealing temperature of 600 °C. Crystalline intensity peaks appeared at 2θ values of 19.80, 31.85, 37.37, 45.19, 56.21, 59.81, 65.69, 67.85, 75.17, and 78.05°. These peaks corresponded to (111), (220), (311), (400), (422), (511), (440), (531), (620), and (622) diffraction planes, respectively, of $MgAl_2O_4$ phase which is characterized from JCPDS card as face-centered cubic, space group, Fd3 m, lattice parameter (a): 8.086, coordination number (Z): 8, and the melting point: 2,135 °C. Other impurity peaks were found for periclase MgO phase (JCPDS card # 45-0946) at 2θ values of 43.37°, 62.93°, 37.25°, and 79.01°. By increasing the annealing temperature to 800, and then to 1,000 °C, a well-formed crystalline of spinel magnesium aluminate phase was obtained. The crystallite sizes of formed single-phase $MgAl_2O_4$ nanopowders was calculated from XRD analyses using Debye–Scherrer formula of the most intense peaks (311) plane and were in the range of 25.30, 31.78, and 33.17 nm at annealing temperature 600, 800, and 1,000 °C, respectively as shown in Table 1. In comparison, the formed nanocrystalline magnesium aluminate spinel phases synthesized using ammonium hydrogen carbonate (NH_4HCO_3) at different pH values from 8 to 11 and annealing temperature from 400 to 1,100 °C for 2 h. The XRD patterns showed that the powder calcined at 400–700 °C corresponded to periclase (MgO) phase (JCPDS, 45-946), decomposed from hydrotalcite. When the sample was heated to 800 °C, the XRD spectra exhibited broadened diffraction peaks indicating the nanocrystalline nature. All the peaks were perfectly indexed to crystalline $MgAl_2O_4$ (JCPDS card # 21-1152). Moreover, the crystallite sizes of the powders were between 10 and 30 nm [15]. So, the advantage of our procedure is that a well nanocrystalline spinel phase can be obtained at low annealing temperature of 600 °C using TEAOH as organic precipitated precursor.

The specific surface area of the produced magnesium aluminate spinel powders was determined by means of the Brunauer–Emmett–Teller (S_{BET}) method. Table 2 revealed the change in the densities and surface areas of the produced aluminates samples as the function of the annealing temperature. The results indicated that the density increased and the surface area decreased with increasing annealing temperature of the magnesium aluminate complex precursors from 600 to 1,000 °C. The results can be attributed to the increase in the average crystallite size of the produced magnesium aluminate spinel powders corresponding with the increse in the annealing temperature, as a result of increase in both the nucleation and growth rates of the produced powders. Maximum surface area can be obtained (182.12 m^2/g) for the powders prepared at 600 °C with HQ. Such high surface area spinel particles are attractive for catalysts and sensors where the catalytic efficiency and the sensitivity improved by developing ultrafine particles with high S_{BET}. The value of surface area of the produced magnesium aluminate spinel powders was higher than those mentioned in the literature for $MgAl_2O_4$ spinel synthesized by solid-state synthesis (37 m^2/g) using MgO and γ-Al_2O_3 annealed at 900 °C for 24 h, mechanochemical synthesis (117 m^2/g), and co-precipitation method (108 m^2/g) using aluminum and magnesium nitrates with ammonia solution as precipitating compounds at pH 11 and annealing temperature of 800 °C for 4 h [33]. In comparison with other study, the surface area of the produced spinel by sonochemical synthesis was between 214.6 and 267.3 m^2/g for

Table 2 Density and specific surface area S_{BET} of the produced $MgAl_2O_4$ powders prepared at different annealing temperatures using TEAOH and HQ as co-precipitating agents

Temperature, °C	Density, g/cm^3		Surface area, m^2/g	
	With TEAOH	With HQ	With TEAOH	With HQ
600	2.612	2.883	95.17	182.12
800	3.369	3.425	60.32	59.67
1,000	3.398	3.491	56.98	59.56

the sample treated at 500 °C and 95.9–110 m^2/g for the sample annealed at 800 °C. The change was dependent on the sources of aluminum and magnesium and addition of cetyltrimethyl ammonium bromide (CTAB) which was treated with ammonia solution at pH 9 and sonicated at 80% of the maximum power, for 8 h.

The microstructure of the magnesium aluminate particles synthesized at annealing temperature 1,000 °C for 2 h was characterized using SEM images (Fig. 3). The sample prepared by TEAOH (Fig. 3a, b) appeared as well-defined morphology with particles sizes that were in the sub-micron range. SEM micrographs also showed that the formed $MgAl_2O_4$ appeared as spherical particles that were interconnected. On the other hand, SEM images (Fig. 3c, d) of the powder produced in the presence of HQ showed that the grains were round with small rodlike-shaped particles.

The particle size distributions (PSD, number,%) of the produced powders annealed at 800 and 1,000 °C for 2 h using TEAOH and HQ dispersed in water are given in Table 3 and Fig. 4. The effects of the annealing temperature and type of organic precipitating compounds on the mean diameter, median (50% of the sample fraction passed), D10 (10% of the sample passed), D75, and D90 was obtained. The results indicated that the average mean diameter of the produced magnesium aluminate powders using TEAOH was 103–104 nm whereas the mean diameter of the produced powders using HQ was 3.469 and 4.641 μm at the annealed temperatures of 800 and 1,000 °C, respectively. Moreover, 10% of the sample was 57 nm in the presence of TEAOH and it became 1.793 and 2.151 μm at annealed temperatures of 800 and 1,000 °C, respectively. In addition (50% of the sample passed) was 0.089 μm and it had the values of 2.666 and 3.472 μm at the studied annealed temperatures, respectively. Then, the results conclusively revealed that the produced magnesium aluminate spinel powders when dispersed in water and measured by LSA were agglomerated in the presence of HQ compared with TEAOH. Moreover, the annealing temperatures have non-significant changes on the particles produced using TEAOH. The agglomerated particles in the presence of HQ than TEOH were related to many factors such as shape factor, surface area, porosity, and density. Furthermore, in a colloidal system, consisting of a large number of small particles in a suspending fluid, particles will collide with one another in the course of their Brownian motion. The aggregate may continue to grow, becoming less mobile, until it settles. Individual particles can only remain in such

Table 3 Particle size distribution (PSD) parameters of the produced $MgAl_2O_4$ powders annealed at 800 and 1,000 °C for 2 h using TEAOH and HQ

Particle size, number, %, μm	With TEAOH		With HQ	
	800 °C	1,000 °C	800 °C	1,000 °C
Mean diameter	0.104	0.103	3.469	4.641
Median	0.089	0.089	2.666	3.472
D10	0.057	0.057	1.793	2.151
D25	0.070	0.070	2.092	2.565
D75	0.120	0.119	3.749	5.093
D90	0.165	0.163	5.619	8.133

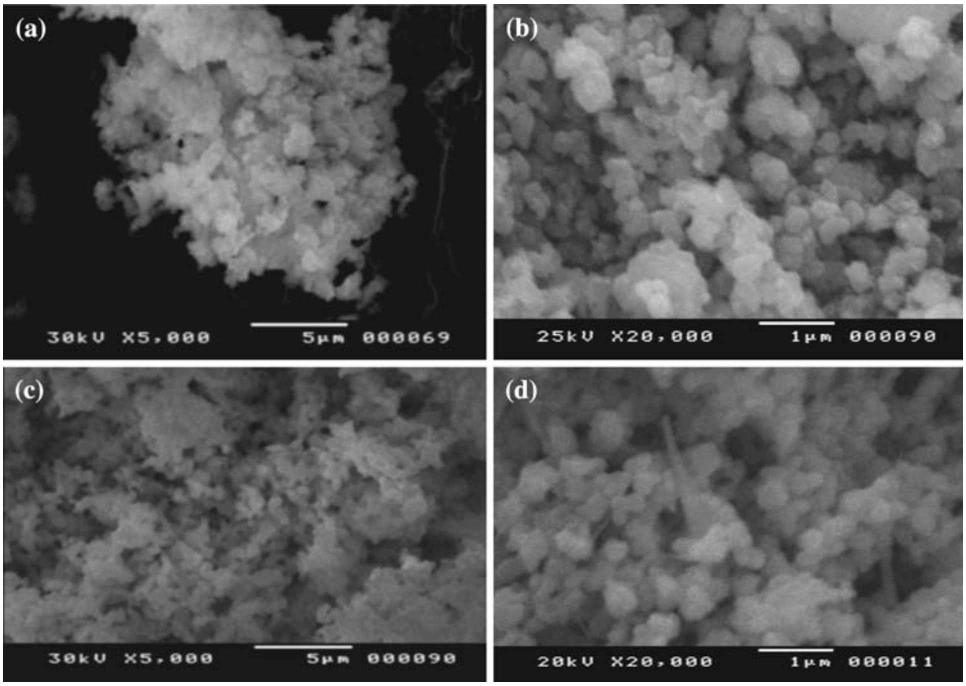


Fig. 3 SEM micrographs of the produced magnesium aluminate spinel powders annealed at 1,000 °C for 2 h using (**a** and **b**) TEAOH (**c** and **d**) HQ

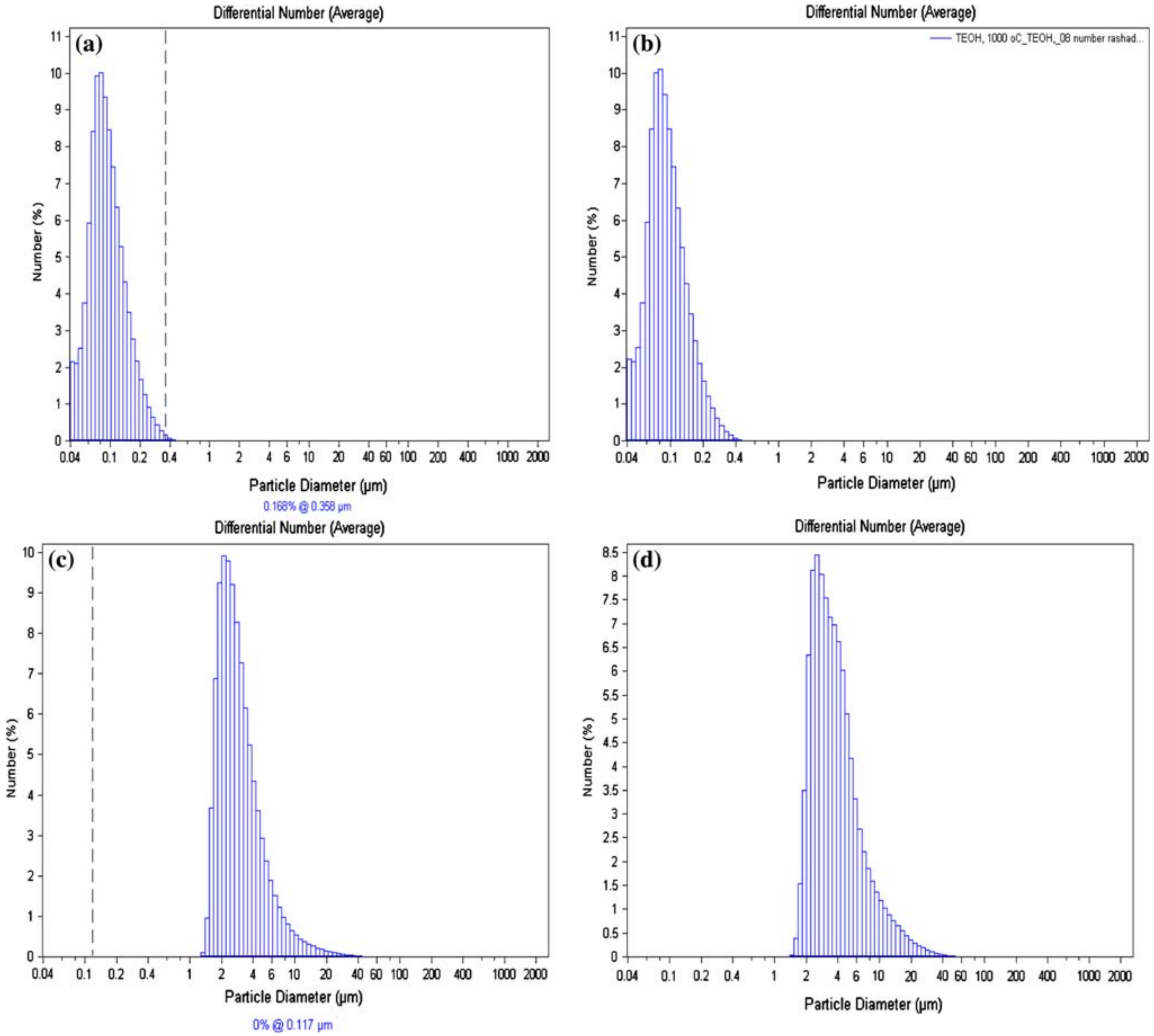


Fig. 4 Particle size distribution PSD of the produced MgAl2O4 powders synthesized by **a** TEAOH at 800 °C **b** TEAOH at 1,000 °C **c** HQ at 800 °C **d** HQ at 1000 °C

systems if there is some mechanism to prevent them from sticking together when they collide with one another. The system is then said to be colloidally stable. One way of producing stability is to give the particles an electric charge (either positive or negative); if all particles have the same charge, they will repel one another on close approach. This is known as "electrostatic stabilisation". A system is colloidally unstable if collisions lead to the formation of aggregates (coagulation or flocculation). Since, when a system changes from being stable to unstable, most of its properties, e.g., settling, filtration, and flow behaviour change, the control of colloidal stability is of great interest. Most colloidal particles are electrically charged, e.g., most metal oxides have a surface layer of the metal hydroxide which is amphoteric and can become either positively or negatively charged, by taking up a proton or by proton abstraction, depending on the pH. The electrostatic potential on the particle surface, relative to the surrounding fluid, is strongly dependent on the balance between the positive and negative ions. For the oxide systems, and many other colloids, the H^+ and OH^- ions are the potential-determining ions. In such systems, the surface charge and potential are determined largely by the balance between H^+ and OH^- in solution, i.e., by the pH [34].

Conclusion

The observations from XRD, SEM, S_{BET} specific surface area, and laser diffraction analyzer (LDA) studies are summarized as follows:

- Single nanocrystalline $MgAl_2O_4$ spinel powders have been synthesized by co-precipitation method using 8-hydroxylquinoline (HQ) and TEAOH.
- The average crystallite size of the produced magnesium aluminate spinel powders was in the range between 8 and 33 nm.
- The lattice parameters for the spinel particles were changed according to different organic precipitating compounds used.
- The surface area of the produced powders decreased with increase in the annealing temperature from 600 to 1,000 °C; maximum surface area can be obtained (182.12 m^2/g) for the powders prepared at 600 °C with HQ. Such high surface area spinel particles are attractive for catalysts and sensors.
- The microstructure was influenced by changing the organic precipitating compounds. The produced $MgAl_2O_4$ annealed at 1,000 °C using TEAOH had spherical shape whereas the produced powders using HQ had round with small rodlike structure.
- The particle size distribution parameters (PSDs) of the produced magnesium aluminate powders when dispersed in water and measured by LSA was agglomerated in the presence of HQ compared with TEAOH.

References

1. Li J-G, Ikegami T, Lee J-H, Mori T, Yajima Y (2001) Ceram Int 27:481
2. Reveron H, Campos DG, Rodriguez RM, Bonassin JC (2002) Mater Lett 56:97
3. Kingery WD, Uhlmann DR (1976) Introduction to ceramics. Wiley, New York
4. Dericioglu AF, Kagawa Y, European J (2003) Ceram Soc 23:951
5. Shimizu Y, Arai H, Seiyama T (1985) Sens Actuators 7:11
6. Gusmamo GMG, Travera E, Bearzotti A (1993) Sens Actuators B 1314:525
7. Ji-Guang L, Ikegami T, Jong-Heun L, Mori T (2000) J Am Ceram Soc 83(11):2866
8. Alinejad B, Sarpoolaky H, Beitollahi A, Saberi A, Afshar S (2008) Mater Res Bull 43:1188
9. Gritsyna VT, Kazarinov YuG, Kobyakov VA, Reimanis IE (2006) Nucl Instrum Methods Phys Res B 250:342
10. Alinejad B, Sarpoolaky H, Beitollahi A, Saberi A, Afshar S (2008) Mater Res Bull 43:1188
11. Iqbal MJ, Farooq S (2007) Mater Sci Eng B 136:140
12. Guo J, Lou H, Zhao H, Wang X, Zheng X (2004) Mater Lett 58:1920
13. Zawrah MF, Hamaad H, Meky S (2007) Ceram Inter 33:969
14. Wajler A, Tomaszewski H, Drożdż-Cieśla E, Węglarz H, Kaszkur Z (2008) J Eur Ceram Soc 28:2495. doi:10.1016/jeurceramsoc.2008.03.013
15. Duan XL, Song CF, Wu YC, Yu FP, Cheng XF, Yuan DR (2008) J Non-Cryst Solids 354:3516
16. Dawson WJ (1988) Ceram Bull 67:1673
17. Andeen D, Loeffler L, Padture N, Lange FF (2003) J Cryst Growth 259:103
18. Ganesh I, Johnson R, Rao GVN, Mahajan YR, Madavendra SS, Reddy BM (2005) Ceram Int 31:67
19. Meyer F, Dierstein A, Beck CH, Härti W, Hempelmann R, Mathur S, Veith M (1999) Nano Struct Mater 12:71
20. Saberi A, Fard FG, Sarpoolaky H, Porada MW, Gerdes T, Simon R (2008) J Alloys Compds 462:142. doi:10.1016/J.jallcom.2007.07.101
21. Ianoş R, Lazău I, Păcurariu C, Barvinschi P (2008) Mater Res Bull 43:3408
22. Păcurariu C, Lazău I, Ecsedi Z, Lazău R, Barvinschi P, Mărginean G (2007) J Eur Ceram Soc 27:707
23. Haijun Z, Xiaolin J, Yongjie Y, Zhanjie L, Daoyuan Y, Zhenzhen L (2004) Mater Res Bull 39:839
24. Pan XL, Sheng SS, Xiong GX, Fang KM, Tudyka S, Stroh N, Brunner H (2001) Colloids Surf A Physicochem Eng Asp 179:163
25. Wang CT, Lin LS, Yang SJ (1992) J Am Ceram Soc 75:2240
26. Yalamac E, Akkurt S, Ciftcioglu M (2003) Key Eng Mater 264–268:53
27. Domanski D, Urretavizcaya G, Castro FJ, Gennari FC, Am J (2004) Ceram Soc 87:2020
28. Rashad MM, Radwan M, Hessien MM (2008) J Alloys Compd 3:304
29. Iqbal MI, Ashiq MN (2008) Chem Eng J 136:383
30. Iqbal MI, Ashiq MN, Gomez PH, Munoz JM (2008) J Magn Magn Mater 320:881
31. Hessien MM, Rashad MM, El-Barawy K (2008) J Magn Magn Mater 320:336
32. Bassett J, Denney RC, Jeffery GH, Mendham J (1978) Vogel's textbook of quantitative inorganic chemistry. Longman, London
33. Bocanegra SA, Ballarini AD, Scelza OA, de Miguel SR (2008) Mater Chem Phys 111:534
34. Allen E, Henshaw J, Smith P (2001) A review of agglomeration. US Department of Energy