# Synthesis of magnesium aluminate spinel nanocrystallites by co-precipitation as function of pH and temperature

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**Abstract.** Magnesium aluminate ($MgAl_2O_4$) spinel nanocrystallites are prepared through nitrate route with liquor ammonia as a precipitant by co-precipitation process. By varying the solution pH (8–10) and bath temperature (10–40°C), the precipitated gel materials are obtained. Yield of each batch is determined by firing at 1000°C with 2 hours (h) soaking. The yield is maximum at 30°C and pH 9.2. Chemical analysis indicates near stoichiometric spinel at pH 9.2. Below pH 9.2, $Al_2O_3$:MgO molar ratio shifts to alumina side; beyond pH 9.2, it is towards magnesia side. Stoichiometric spinel-forming precursor material is characterized by various techniques. X-ray diffraction (XRD) analysis indicates spinel formation at 600°C and its crystallinity increases with rise of temperature. Hydroxyl group and absorbed water in gel substrate disappear with variation of temperature as observed by Fourier transform infrared (FTIR). Only one exothermic response of the precursor of spinel formation is demonstrated through differential scanning calorimetry (DSC). Studies reveal formation of near stoichiometric magnesium aluminate spinel powder having average crystalline size in the range 15–38 nm. HR-transmission electron microscopy studies also confirm this nano-size crystallite formation.

**Keywords.** Magnesium aluminate; co-precipitation; yield; crystallites; stoichiometric.

## 1. Introduction

Bottom-up approach that deals with the crucial role of pH and temperature is significant when co-precipitation technique is used for the preparation of $MgAl_2O_4$ (spinel) nanoparticles. This ceramic material has outstanding multipurpose properties and has been generating interest among researchers. The high melting point (2135°C), mechanical strength at elevated temperatures, chemical inertness and good thermal shock resistance are substantial properties, which permit $MgAl_2O_4$'s use in different applications such as fusion reactors, cement rotary kilns, steel ladles and support as catalyst in the field of environmental catalysis, etc. Now, to synthesize stoichiometric $MgAl_2O_4$ (spinel), the main challenge is to design a method that will give precursor powder with $Mg^{2+}$:$Al^{3+}$ ionic ratio as 1:2. Considering the processing challenges, numerous techniques such as co-precipitation [1–9], sol–gel [10, 11], spray drying [12], spray pyrolysis [13], bicarbonate precursor method [14], citrate–nitrate combustion method [15], microwave-assisted combustion synthesis [16], etc. were used by researchers in making spinel-forming precursor powder.

Among the different wet chemical techniques, co-precipitation is one of the best in terms of low cost, high purity and volume production. To prepare Mg–Al spinels, co-precipitation has been applied by researchers with various combinations of aluminium- and magnesium-based inorganic salts such as nitrates, chlorides, sulphates, etc.

In the present investigation, co-precipitation method by nitrate route has been used to synthesize spinel. The objectives of this study are to (a) investigate the optimum co-precipitation conditions (pH, temperature) to obtain maximum yield, (b) determine alumina and magnesia contents of the dried co-precipitated powders formed at 30°C at different pH values, viz. 8, 8.5, 9, 9.2, 9.5 and 10 and (c) characterize the precursor powder formed at pH 9.2 by different instrumental techniques such as differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and HR-transmission electron microscopy (HR-TEM).

## 2. Experimental

### 2.1 *Powder preparation*

In the present study, A.R. grade aluminium nitrate-non-ahydrate [$Al(NO_3)_3 \cdot 9H_2O$] and magnesium nitrate-

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hexahydrate [$Mg(NO_3)_2 \cdot 6H_2O$] were used as sources of alumina and magnesia, respectively. Ammonia solution (1:1) was used as the precipitant. Three sets of salt solutions – (i) aluminium nitrate of strength 0.3 M, (ii) magnesium nitrate of strength 0.15 M and (iii) mixed salt solution of strength 0.3 M with respect to $Al(NO_3)_3$ and 0.15 M with respect to $Mg(NO_3)_2$ were made separately.

A small batch size of 100 ml mixed salt solution was taken in a 250 ml beaker; ammonia solution (1:1) was slowly added with constant stirring by a magnetic stirrer until pH attained the value 8.0 and kept for 5 min. During precipitation, temperature was maintained at 30°C. The precipitate was filtered through Whatman No 41 filter paper, washed thoroughly with deionized water and quantitatively estimated by calcining at 1000°C for 2 h. Yield was calculated from weight of calcined precipitate and weight of equivalent $Al_2O_3+MgO$ present in 100 ml mixed salt solution. The same experiments were repeated at other pH, viz. 8.5, 9.0, 9.2, 9.5 and 10. Similar experiments were conducted at 30°C for other two sets of solutions for determination of yield at different pH for alumina and magnesia.

For mixed solution, co-precipitation was repeated at pH 9.2 at different temperatures, viz. 10, 15, 20, 25, 35 and 40°C. Yield was calculated in each case. Variation of pH in all cases was ±0.05 and temperature ±1°C. Flow diagram of co-precipitation process is shown in figure 1.

## 2.2 *Powder characterization*

Conventional wet chemical method was used to determine $Al_2O_3$ and MgO content of precipitate formed at 30°C with variation of pH values. The 110°C dried powder was analysed through DSC (NETZSCH 404 F1 Pegasus) at the following heating rates, viz. 5, 10 and 15°C/min. FTIR (SHIMADZU-IR AFFINITY-1) spectra of gel and calcined powders at different temperatures were obtained in the scan range 400–4000 $cm^{-1}$. Dried (110°C) and calcined powders were analysed by XRD (BRUKER D8 ADVANCED) through Cu-Kα radiation. The crystallite size of calcined powders was investigated by HR-TEM (FEI-Tecnai $G^2$ 20).
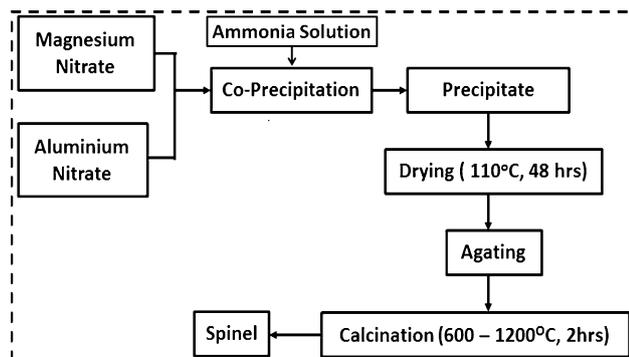


**Figure 1.**   Flow diagram of co-precipitation process.

# 3. Results and discussion

## 3.1 *Influence of pH and temperature on precipitation*

The yield of co-precipitate increases with pH and reaches a maximum value at pH 9.2. Beyond 9.2 it decreases, as shown in table 1.

Similar behaviours have been observed during precipitation of $Al(OH)_3$ from $Al(NO_3)_3$ solution, where yield reaches a maximum value close to pH 8.0 and later decreases due to dissolution of a portion of $Al(OH)_3$ as aluminate beyond pH 8.0 (table 2).

In contrast, $Mg(OH)_2$ starts precipitating at higher pH (approximately 8.0) from $Mg(NO_3)_2$ solution; its yield increases with pH and attains a maximum value at pH 10.0 (table 2). Since $Mg(OH)_2$ is basic in nature, there will be no dissolution of $Mg(OH)_2$ at higher pH. It is interesting to note that yield values of $Al(OH)_3$ and $Mg(OH)_2$ from individual nitrate solutions become nearly identical at pH 9.2, revealing molar ratio of $Al(OH)_3$ and $Mg(OH)_2$ as $Al_2O_3$:MgO to be a little above 1 since 100 ml of 0.3 M $Al(NO_3)_3$ and 100 ml of 0.15 M $Mg(NO_3)_2$ solutions evolve equimolar $Al_2O_3$ and MgO. For better understanding, the same yield value in the close pH range (9–9.5) has been plotted in figure 2.

From this figure it is evident that stoichiometric yield of 95% is obtained at pH 9.22. This observation gives an idea that the co-precipitate formed at pH 9.22 should give near stoichiometric spinel on calcination. Some authors [1–3, 7–9] reported that the co-precipitate formed at pH 9.2 forms stoichiometric spinel, and at higher pH, i.e. pH

**Table 1.**   Variation of yield (wt%) of co-precipitate formed at different pH at 30°C.

| pH | Yield (wt%) |
|----|-------------|
| 8.0 | 72.5 |
| 8.5 | 79.0 |
| 9.0 | 89.2 |
| 9.2 | 95.0 |
| 9.5 | 92.5 |
| 10.0 | 90.3 |

**Table 2.**   Variation of yield [wt% $Al_2O_3$ from $Al(NO_3)_3$ solution and wt% MgO from $Mg(NO_3)$ solution] with pH at 30°C.

| pH | $Al^{3+}$ solution + ammonia solution yield (wt%) | $Mg^{2+}$ solution + ammonia solution yield (wt%) |
|----|------|------|
| 8.0 | 99.1 | 5.6 |
| 8.5 | 98.2 | 30.2 |
| 9.0 | 96.4 | 73.0 |
| 9.2 | 95.4 | 94.1 |
| 9.5 | 90.2 | 98.2 |
| 10.0 | 87.0 | 98.6 |

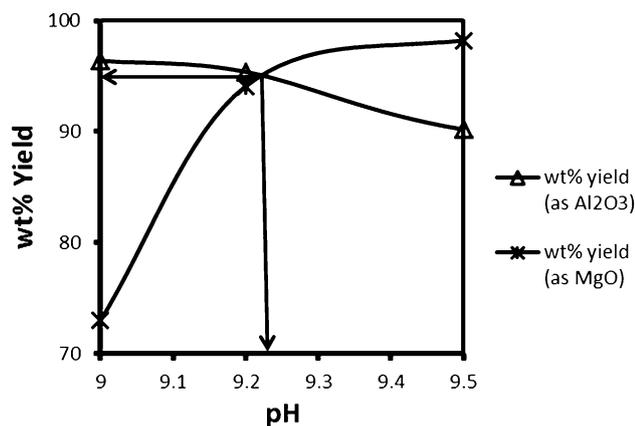**Figure 2.** Variation of yield [wt% $Al_2O_3$ from $Al(NO_3)_3$ solution and wt% MgO from $Mg(NO_3)_2$ solution] in the close pH range at 30°C.

9.5–10.0, it becomes magnesia-rich spinel. Also, a few authors [6] reported stoichiometric spinel formation in the pH range 9.5–10.0. Our findings indicate stoichiometric spinel formation at pH 9.22. Chemical analysis of precursor powders formed at 30°C in a range of pH (8.0–10.0) is shown in table 3.

From table 3 we find that precipitation of $Mg^{2+}$ as $Mg(OH)_2$ starts at around pH 8.0, where its value as MgO is 2.34 wt% on loss-free basis. This value gradually rises with increasing pH and reaches a maximum value of 30.79 wt% at pH 10.0. Results also indicate stoichiometric spinel formation at a specific pH between 9.2 and 9.5, which matches with the yield values from individual nitrates. Temperature has some effect on yield during co-precipitation at pH 9.2 (table 4). Results show that the maximum yield is obtained in 25–30°C temperature range.

### 3.2 *DSC analysis*

DSC analysis of the 110°C dried gel was performed at different heating rates, as shown in figure 3.

The DSC traces of samples exhibit a single exothermic peak in the temperature range of 600–700°C, which could be attributed to the formation of spinel. Usually, the exothermic peaks shift to higher temperature with

**Table 4.** Variation of yield (wt%) with temperature of co-precipitate formed at pH 9.2.

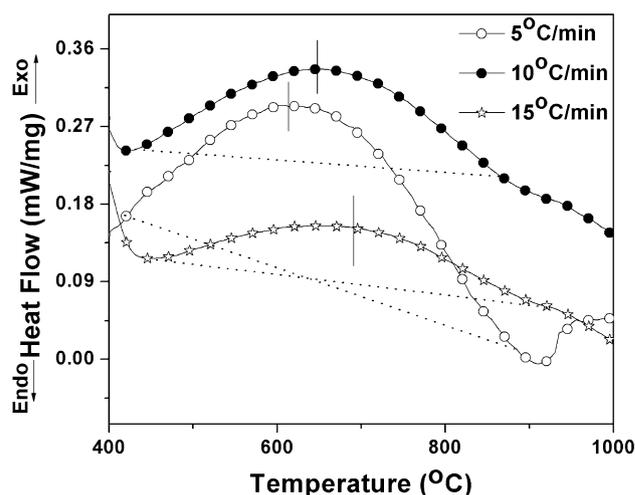| Temperature (°C) | Yield (wt%) |
|---|---|
| 10 | 78.3 |
| 15 | 86.2 |
| 20 | 89.9 |
| 25 | 94.4 |
| 30 | 95.0 |
| 35 | 87.5 |
| 40 | 86.8 |



**Figure 3.** DSC curves of the 110°C dried gel at different heating rates (5, 10 and 15°C/min).

increasing heating rates. Further, the peak areas decrease as heating rate increases due to the suppression of diffusion process. The formation rate of spinel gets inhibited at higher heating rates, possibly due to its lower reaction time.

### 3.3 *FTIR analysis*

Figure 4 shows the FTIR spectra of precursor gel and calcined samples. The FTIR spectrum of precursor gel shows a broad peak around 3400 $cm^{-1}$, which is due to the presence of hydroxyl group and absorbed water in gel. Also, the peak at

**Table 3.** Chemical analysis of spinel-forming precursor formed at different pH and 30°C.

| pH | Chemistry of precursor powder dried at 110°C | | | Chemistry of precursor powder (loss-free basis) | | |
|---|---|---|---|---|---|---|
| | $Al_2O_3$ (wt%) | MgO (wt%) | Loss on ignition (1000°C, 2 h) (wt%) | $Al_2O_3$ (wt%) | MgO (wt%) | Molar ratio of $Al_2O_3$:MgO |
| 8.0 | 47.62 | 1.14 | 50.90 | 97.66 | 2.34 | 16.37 |
| 8.5 | 43.92 | 5.22 | 50.46 | 89.37 | 10.63 | 3.30 |
| 9.0 | 39.50 | 11.35 | 48.65 | 77.68 | 22.32 | 1.36 |
| 9.2 | 36.76 | 14.18 | 48.36 | 72.17 | 27.83 | 1.02 |
| 9.5 | 36.95 | 15.76 | 46.80 | 70.08 | 29.92 | 0.92 |
| 10.0 | 37.91 | 16.87 | 44.73 | 69.21 | 30.79 | 0.88 |
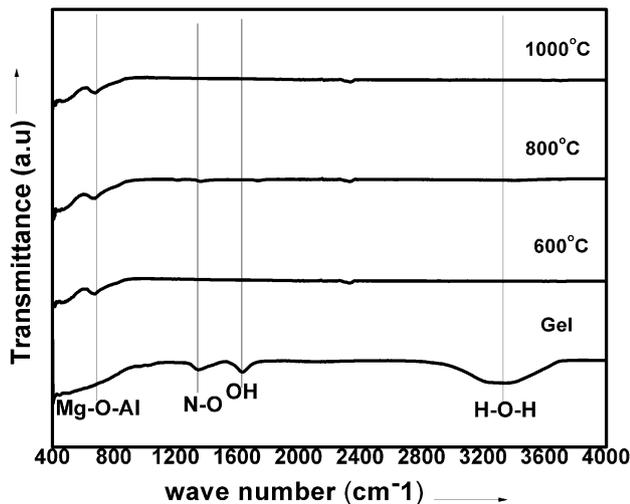
**Figure 4.** FTIR spectra of precursor gel and calcined samples.



**Figure 5.** X-ray diffraction patterns of samples dried at 110°C and calcined at different temperatures (600–1200°C).

$1630$ cm$^{-1}$ is related to water. For the calcined samples, an additional peak is observed at $660$ cm$^{-1}$, which is not present in the FTIR spectrum of precursor cake. In the spectra of the sample calcined at different temperatures the peak at $660$ cm$^{-1}$ is due to Mg–O–Al linkages, and it becomes distinct with temperature of calcination due to better crystallization at higher temperatures. The peak at $1340$ cm$^{-1}$ is of N–O group and the peak close to $2370$ cm$^{-1}$ is probably because of propagation of IR beam in air.

### 3.4 *XRD evaluation*

Figure 5 shows the XRD patterns of samples dried at 110°C and calcined at different temperatures varying from 600 to 1200°C with 2 h soaking. Before calcination, there are no peaks due to amorphous nature of precipitates. After calcination, $MgAl_2O_4$ (spinel) peaks are observed close to $2\theta$ values of 37°, 46°, 61° and 66°, which correspond, respectively, to (311), (400), (511) and (220) reflection (JCPDS no 21-1152). The XRD curve at 600°C indicates spinel formation, which is also evidenced from DSC studies with heating rate 5°C/min and FTIR analysis of the powder calcined at 600°C. The XRD curve of powder calcined at 1200°C shows a weak $\alpha$-$Al_2O_3$ peak due to precipitation of $\alpha$-$Al_2O_3$ from spinel containing a little excess alumina as $\gamma$-$Al_2O_3$ in stoichiometric spinel structure. Chemical analysis of precursor powder formed at pH 9.2 and 30°C (table 3) shows molar ratio of $Al_2O_3$:MgO as 1.02:1, indicating that spinel contains 1.44 wt% excess alumina beyond stoichiometry and it exsolves out as $\alpha$-$Al_2O_3$ at 1200°C with 2 h soaking, which is also reported [9].

The average crystallite size was calculated using Scherrer's formula for the peak at 37°C as follows:
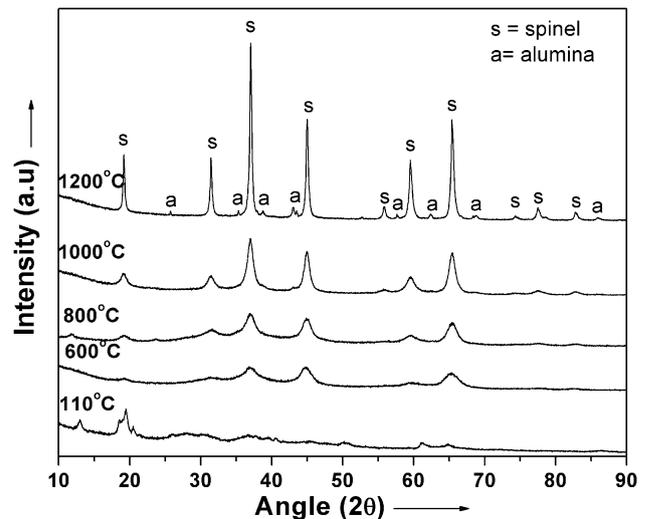
$$D = \frac{0.9\lambda}{B \cos\theta} \tag{1}$$

**Table 5.** Average crystalline size samples calcined at 600–1200°C using Scherrer's formula.

| Calcination temperature (°C) | 600 | 800 | 1000 | 1200 |
|---|---|---|---|---|
| Average crystallite size (nm) | 15 | 33 | 36 | 38 |

where $\lambda$, $B$ and $\theta$ are the wave length, full-width at half-maximum intensity and Bragg angle of the X-ray, respectively. The bigger sizes of the crystallites obtained at higher calcination temperatures are due to the thermally assisted crystallite formation. The size of the spinel crystallites increases from 15 to 38 nm when the calcination temperature is raised from 600 to 1200°C (table 5).

### 3.5 *HR-TEM analysis*

To investigate the effect of calcination temperature on the formation of spinel, the structural properties of the specimens have been studied by HR-TEM. The powder samples were made ready by grinding the neutron-irradiated samples on a diamond film, followed by scattering of the *powder* in isopropyl alcohol on a carbon grid. HR-TEM images and their corresponding SAED patterns of spinel obtained at 600, 800, 1000 and 1200°C temperatures are depicted in figure 6(a), (b), (c), (d), (e), (f), (g) and (h), respectively.

From figure 6(a, c, e, g), it has been observed that crystallite size in the soft agglomerates increases with rise in calcination temperature, which is also confirmed from XRD studies. Furthermore, SAED patterns reveal clear spots at 1000°C compared with 600 and 800°C, indicating more crystallinity. From figure 6(e, g), we find that the average crystallite size is in the range 35–38 nm approximately. Also, the uniform SAED diffraction patterns give the interpretation that nanocrystallites are in abundance.
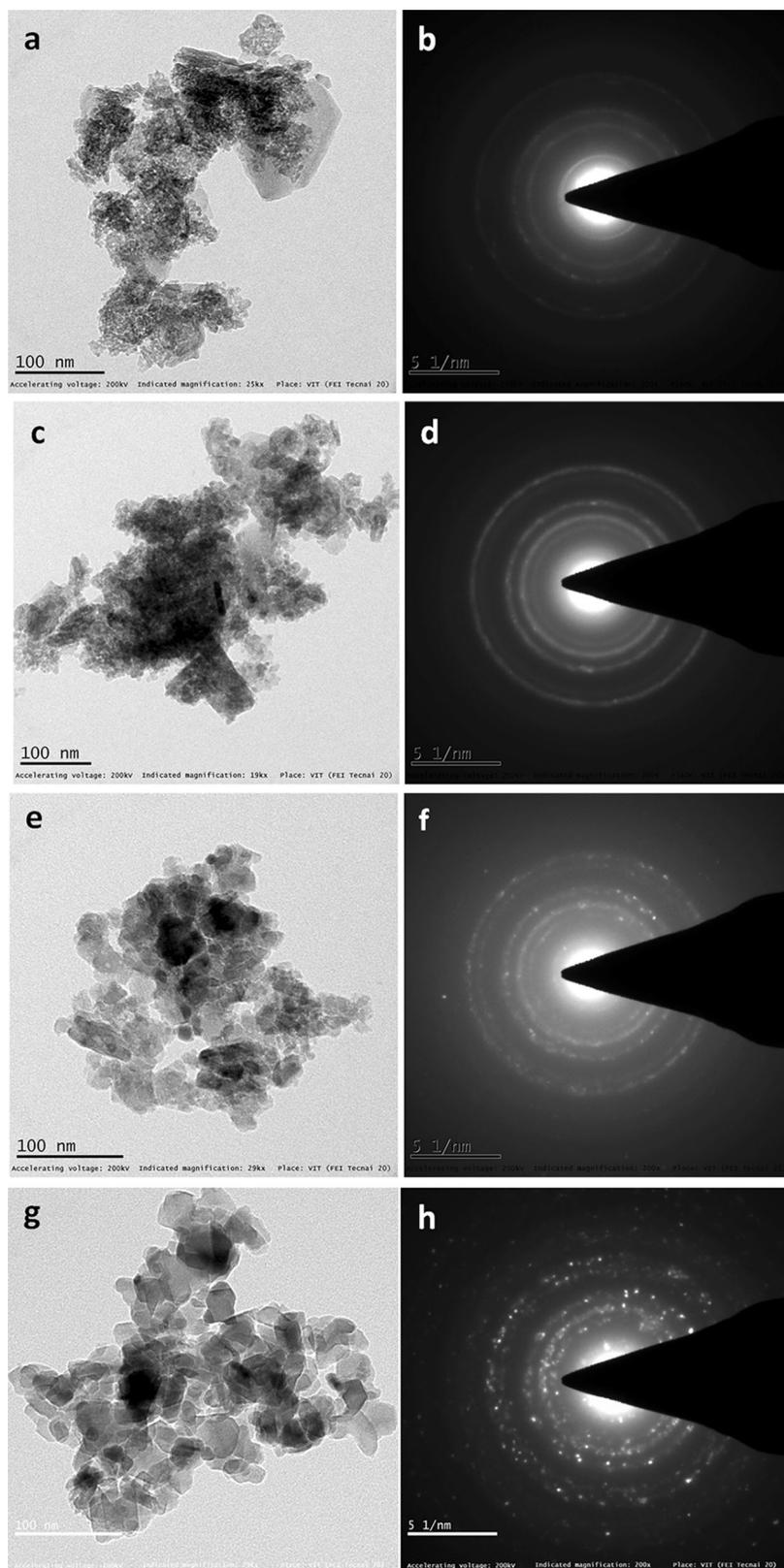
**Figure 6.** HR-TEM images with SAED patterns of samples calcined at 600°C (**a**, **b**); 800°C (**c**, **d**); 1000°C (**e**, **f**) and 1200°C (**g**, **h**).

## 4. Conclusions

Co-precipitation technique through nitrate route forms near stoichiometric spinel-forming precursor hydrate having yield above 90% at pH 9.2 and temperature 25–30°C. DSC analysis indicates only one spinel-forming exothermic peak around 600°C and the value shifts to 700°C when heating rate changes from 5 to 15°C/min. The DSC analysis indicates that the peak area decreases with increasing heating rate, which is due to the suppression of Al and Mg diffusion. Formation of reactive and non-reactive groups (O–H, H–O–H, Mg–O–Al) is confirmed by FTIR analysis. XRD studies show complete spinel formation at 600°C, and only spinel peaks with powder calcined up to 1000°C, having exception at 1200°C, where weak peaks of $\alpha$-$Al_2O_3$ appear due to exsolution of excess alumina present as $MgAl_2O_4$–$\gamma$-$Al_2O_3$ solid solution in spinel structure. Chemical analysis also suggests the fact that precursor powder has $Al_2O_3$:-MgO molar ratio 1.02:1.0. This concludes that some excess alumina beyond spinel stoichiometry exists in spinel structure as $MgAl_2O_4$–$\gamma$-$Al_2O_3$ solid solution. HR-TEM of spinel powders calcined at 1000 and 1200°C reveals average crystallite size in the soft agglomerates in the range 35–38 nm, which is also confirmed from XRD results.

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