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The effect of the concentration of citric acid and pH values on the preparation of $MgAl_2O_4$ ultrafine powder by citrate sol–gel process

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Abstract

Ultrafine $MgAl_2O_4$ was synthesized by citrate sol–gel process. A model was presented to evaluate the concentration of species in a citric solution for preparing $MgAl_2O_4$ ultrafine powder. The evaluated concentration of species can provide valuable information and help in selecting the optimal condition for preparation of $MgAl_2O_4$ powder by citrate sol–gel process. The influence of molar ratio of cations, citric acid and pH on the formation of $MgAl_2O_4$ was studied. The spinel precursor gel and the ultrafine $MgAl_2O_4$ spinel were characterized by X-ray diffraction (XRD), differential thermal analysis, thermogravimetric (TG-DTA) and scanning electron microscope (SEM). The results show that the $MgAl_2O_4$ spinel phase begins to form at 600 °C, and most of $MgAl_2O_4$ crystals are spherical with a crystal size about 30–50 nm.

Keywords: A. Nanostructures; A. Inorganic compounds; A. Oxides; B. Sol–gel chemistry; C. X-ray diffraction

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1. Introduction

$MgAl_2O_4$ spinel is the only chemical compound in the binary $MgO–Al_2O_3$ system that possesses a wide range of solid solutions for spinel-corundum compositions. $MgAl_2O_4$ spinel has high-melting point, high chemical inertness against both acidic and basic slags, low expansion values at elevated temperatures, and is an ecologically benign refractory material [1,2]. It has been recognized as one of the effective refractory materials and used in steel ladles, cement rotary kilns, vacuum induction furnaces, continuous casting tundishes, glass industries, etc. [3–5]. The conventional method of

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preparation of $MgAl_2O_4$ spinel is to calcine the mixture of MgO and Al_2O_3 or other raw materials at high temperature, which has disadvantages of large aggregates and inhomogeneous compositions. In recent years, several types of wet-chemical techniques have been successfully used for the preparation of pure spinel powders at relatively low temperatures, such as precipitation [6,7], sol–gel of metal alkoxides [8], spray-drying [9], freeze-drying [10], modified Pechini process [11].

The pechini or citrate process is usually considered to have the advantage of mixing ions on the atomic scale in the liquid state, so it is easy to control accurately the composition of the powder. However, there are many types of cation citrate complexes in the solution, so the concentration of citric acid could affect the formation of citrate complexes and further affect precipitation and segregation during gelling and charring, respectively. In this present paper, the citrate sol–gel process is used to prepare ultrafine $MgAl_2O_4$, and a model is presented to evaluate the influence of the cations and citric acid on the concentration of the cations citrate complexes in solution.

2. Experimental procedure

The raw materials utilized in present paper were analytical reagent grade magnesium nitrate, aluminium nitrate and citric acid. Stoichiometric amounts of magnesium nitrate and aluminium nitrate were dissolved in distilled water, then a stoichiometric amount of citric acid was added. After complete mixing, a homogenous transparent solution was achieved within a few seconds. Ammonia solution (about 1 M) was added drop by drop to change the pH ($pH = 0–5$) to facilitate the formation of a homogeneous solution. The solution was slowly evaporated to form a highly viscous colloid, which was then heated in a temperature range of 120–140 °C for 24 h to get a dried gel. Finally, the dried gel precursor was calcined at different temperatures to obtain ultrafine $MgAl_2O_4$ powder.

Differential thermal and thermogravimetric analysis of precursor were carried out on a NETZSCH STA-449C Thermal Analysis System with increasing temperature rate 10 °C/min in flowing air. The sample weight was 30 mg. The sample pot was platinum with a depth of 5 mm and the reference material was alpha-alumina. X-ray diffraction patterns were recorded from 20 to 70° (2θ) with a step width of 0.02°, using a Philips X'Pert PRO diffractometer with Cu Kα radiation. The apparent crystallite size of the spinel powder was determined using the Scherrer formula. The powder morphology was observed via scanning electron microscopy (SEM) (Model, JSM-5610LV, JEOL, Japan).

3. A model for evaluating the concentration of magnesium and aluminium citrate complexes in a solution under different conditions

In this model, the concentration of citric acid, pH and temperature affecting the formation of magnesium and aluminium citrate complexes have been taken into consideration. Several assumptions involved were that [12],

(1) Solutions were assumed to be ideal.
(2) One citrate ion could form a chelate with only one cation.
(3) Concentration of the complexes did not change as temperature increased.

The concentration at 25 °C was taken as the reference.

The dissociation of the citric acid involving three stages of ionization was written as follows,

$$H_3Cit \leftrightarrow H_2Cit^- + H^+ \quad k_1 = \frac{\lfloor H_2Cit^- \rfloor \lfloor H^+ \rfloor}{[H_3Cit]} = 7.4 \times 10^{-4} \tag{1}$$

$$H_2Cit^- \leftrightarrow HCit^{2-} + H^+ \quad k_2 = \frac{\lfloor HCit^{2-} \rfloor \lfloor H^+ \rfloor}{[H_2Cit^-]} = 1.7 \times 10^{-5} \tag{2}$$

$$HCit^{2-} \leftrightarrow Cit^{3-} + H^+ \quad k_3 = \frac{\lfloor Cit^{3-} \rfloor \lfloor H^+ \rfloor}{[HCit^{2-}]} = 4.0 \times 10^{-7} \tag{3}$$

H_3Cit represents citric acid and k_1, k_2, k_3 are the equilibrium constants of citric acid. Eqs. (1)–(3) could be rewritten as,

$$[H_2Cit^-] = \frac{[Cit^{3-}][H^+]^2}{k_2 k_3} \tag{4}$$

$$[HCit^{2-}] = \frac{[Cit^{3-}][H^+]}{k_3} \tag{5}$$

$$[H_3Cit] = \frac{[Cit^{3-}][H^+]^3}{k_1 k_2 k_3} \tag{6}$$

The hydrolysis of Mg^{2+} can be written as follows,

$$Mg^{2+} + H_2O \leftrightarrow Mg(OH)^+ + H^+ \quad k_7 = \frac{\lfloor Mg(OH)^+ \rfloor \lfloor H^+ \rfloor}{[Mg^{2+}]} = 10^{-4.9} \tag{7}$$

Eq. (7) could be also rewritten as,

$$[Mg(OH)^+] = \frac{\lfloor Mg^{2+} \rfloor k_7}{[H^+]} \tag{8}$$

The hydrolysis of Al^{3+} can be written as follows,

$$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+ \quad k_9 = \frac{\left\lfloor Al(OH)^{2+} \right\rfloor \lfloor H^+ \rfloor}{[Al^{3+}]} = 10^{-4.9} \tag{9}$$

$$Al^{3+} + 2H_2O \leftrightarrow Al(OH)_2^+ + 2H^+ \quad k_{10} = \frac{\lfloor Al(OH)_2^+ \rfloor \lfloor H^+ \rfloor^2}{[Al^{3+}]} = 10^{-9.3} \tag{10}$$

By Eqs. (9) and (10), one obtains,

$$[Al(OH)^{2+}] = \frac{\lfloor Al^{3+} \rfloor k_9}{[H^+]} \tag{11}$$

$$[Al(OH)_2^+] = \frac{\lfloor Al^{3+} \rfloor k_{10}}{[H^+]^2} \tag{12}$$

The formation reaction of Mg(HCit) complex is,

$$\mathrm{Mg}^{2+} + \mathrm{HCit}^{2-} \leftrightarrow \mathrm{Mg(HCit)} \quad k_{13} = \frac{[\mathrm{Mg(HCit)}]}{[\mathrm{Mg}^{2+}][\mathrm{HCit}^{2-}]} = 10^{3.29} \tag{13}$$

Combining Eq. (13) with (5), one obtains,

$$[\mathrm{Mg(HCit)}] = [\mathrm{Mg}^{2+}][\mathrm{Cit}^{3-}][\mathrm{H}^{+}]\frac{k_{13}}{k_5} \tag{14}$$

Similarly, one obtains,

$$\mathrm{Al}^{3+} + \mathrm{HCit}^{2-} \leftrightarrow \mathrm{Al(HCit)}^{+} \quad k_{15} = \frac{\lfloor \mathrm{Al(HCit)}^{+} \rfloor}{[\mathrm{Al}^{3+}][\mathrm{HCit}^{2-}]} = 10^{7} \tag{15}$$

$$\mathrm{Al}^{3+} + \mathrm{Cit}^{3-} \leftrightarrow \mathrm{Al(Cit)} \quad k_{16} = \frac{[\mathrm{Al(Cit)}]}{[\mathrm{Al}^{3+}][\mathrm{Cit}^{3-}]} = 10^{20} \tag{16}$$

$$\mathrm{Al}^{3+} + \mathrm{OH}^{-} + \mathrm{Cit}^{3-} \leftrightarrow \mathrm{Al(OHCit)}^{-} \quad k_{17} = \frac{\lfloor \mathrm{Al(OHCit)}^{-} \rfloor}{[\mathrm{Al}^{3+}][\mathrm{Cit}^{3-}][\mathrm{OH}^{-}]} = 10^{30.6} \tag{17}$$

Combining Eqs. (15–17) with (5), one obtains,

$$[\mathrm{Al(HCit)}^{+}] = [\mathrm{Al}^{3+}][\mathrm{Cit}^{3-}][\mathrm{H}^{+}]\frac{k_{15}}{k_5} \tag{18}$$

$$[\mathrm{Al(Cit)}] = [\mathrm{Al}^{3+}][\mathrm{Cit}^{3-}]k_{16} \tag{19}$$

$$[\mathrm{Al(OHCit)}^{-}] = [\mathrm{Al}^{3+}][\mathrm{Cit}^{3-}]\frac{k_{17}k_w}{[\mathrm{H}^{+}]} \quad (k_w = 10^{-14}) \tag{20}$$

The total magnesium, aluminium, citrate concentration can be expressed as follows,

$$[\mathrm{Mg}]_{\mathrm{T}} = \lfloor \mathrm{Mg}^{2+} \rfloor + \lfloor \mathrm{Mg(OH)}^{+} \rfloor + [\mathrm{Mg(HCit)}] \tag{21}$$

$$[\mathrm{Al}]_{\mathrm{T}} = [\mathrm{Al}^{3+}] + [\mathrm{Al(OH)}^{2+}] + \lfloor \mathrm{Al(OH)}_2^{+} \rfloor + [\mathrm{Al(HCit)}^{+}] + [\mathrm{Al(Cit)}] + [\mathrm{Al(OH)Cit}^{-}] \tag{22}$$

$$\begin{aligned}[\mathrm{H_3Cit}]_{\mathrm{T}} = {} & [\mathrm{H_3Cit}] + \lfloor \mathrm{H_2Cit}^{-} \rfloor + \lfloor \mathrm{HCit}^{2-} \rfloor + \lfloor \mathrm{Cit}^{3-} \rfloor + [\mathrm{Mg(HCit)}] + \lfloor \mathrm{Al(HCit)}^{+} \rfloor \\ & + [\mathrm{Al(Cit)}] + \lfloor \mathrm{Al(OH)Cit}^{-} \rfloor \end{aligned} \tag{23}$$

where $[\mathrm{Mg}]_{\mathrm{T}}$, $[\mathrm{Al}]_{\mathrm{T}}$, and $[\mathrm{H_3Cit}]_{\mathrm{T}}$ is the total concentration of magnesium, aluminium and citric ions in the solution, respectively.

Substituting Eqs. (8) and (14) into Eq. (21), one obtains,

$$[\mathrm{Mg}]_{\mathrm{T}} = [\mathrm{Mg}^{2+}]\left(1 + \frac{k_4}{[\mathrm{H}^{+}]}\right) + [\mathrm{Mg}^{2+}][\mathrm{Cit}^{3-}][\mathrm{H}^{+}]\frac{k_9}{k_3} \tag{24}$$

Substituting Eqs. (11)-(12), and Eqs. (18)-(20) into Eq. (22), one obtains,

$$[\mathrm{Al}]_{T} = [\mathrm{Al}^{3+}]\left(1 + \frac{k_6}{[\mathrm{H}^{+}]} + \frac{k_7}{[\mathrm{H}^{+}]^2}\right) + [\mathrm{Al}^{3+}][\mathrm{Cit}^{3-}]\left(k_{11} + [\mathrm{H}^{+}]\frac{k_{10}}{k_3}\right) \tag{25}$$

Substituting Eqs. (4)–(6), (14), (18)–(20) into Eq. (23), one obtains,

$$[\mathrm{H_3Cit}]_\mathrm{T} = [\mathrm{Cit^{3-}}]\left(1 + \frac{[\mathrm{H^+}]}{k_3} + \frac{[\mathrm{H^+}]^2}{k_2k_3} + \frac{[\mathrm{H^+}]^3}{k_1k_2k_3}\right) + [\mathrm{Mg^{2+}}][\mathrm{Cit^{3-}}][\mathrm{H^+}]\frac{k_9}{k_3} + [\mathrm{Al^{3+}}][\mathrm{Cit^{3-}}]\left(k_{11} + [\mathrm{H^+}]\frac{k_{10}}{k_3}\right) \qquad (26)$$

4. Results and discussion

Figs. 1–4 show the theoretically calculated magnesium and aluminum complex concentrations at different pH values and concentrations of citric acid. In Figs. 1–3, it indicates that,

(1) the concentration of Mg^{2+} and Al(Cit) ions decreases with increasing pH values, the concentration of Mg(HCit) and $Al(OH)Cit^-$ ions increases with pH values increase;
(2) the concentration of citric acid shows a little influence on the concentration of Mg^{2+} and Mg(HCit) ions, however, it has almost no effect on the concentration of Al(Cit) and $Al(OH)Cit^-$ ions;

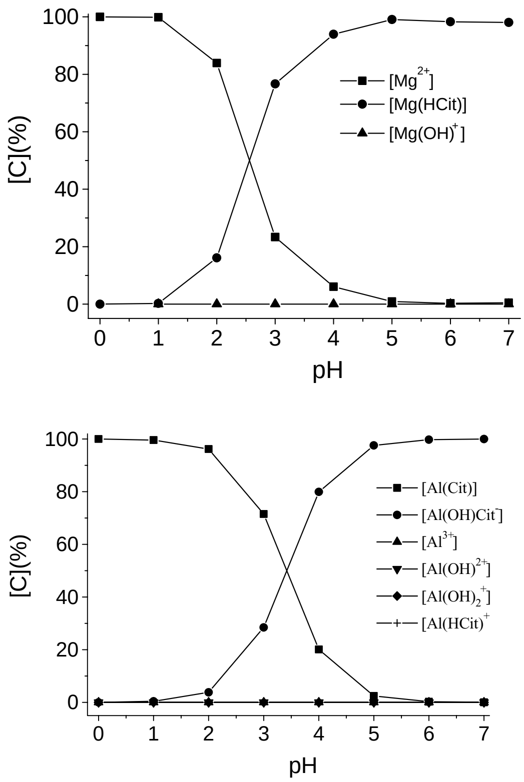


Fig. 1. The evaluated concentration of magnesium species in the solution, in which the molar ratio of citric acid to the total moles of cations is 1:1.

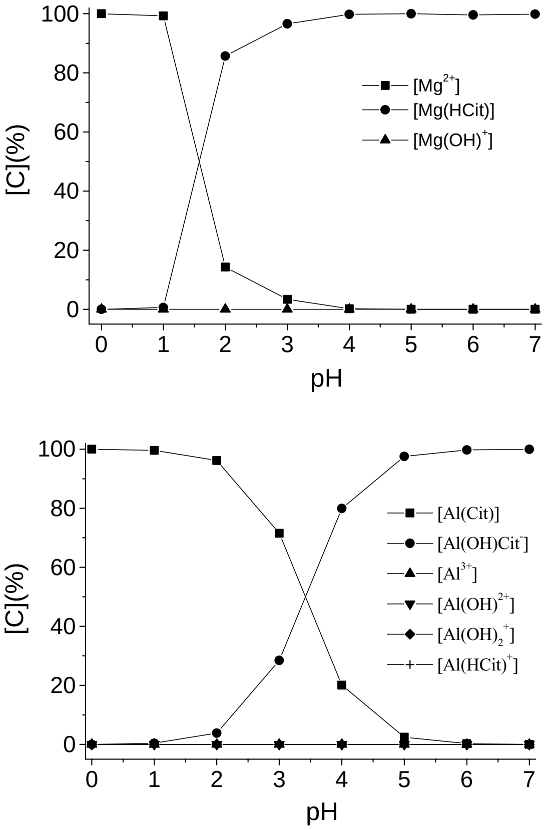


Fig. 2. The evaluated concentration of magnesium species in the solution, in which the molar ratio of citric acid to the total moles of cations is 2:1.

(3) the concentration of $Mg(OH)^{+}$, Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2{}^{+}$, $Al(HCit)^{+}$ ions is lower with a value about 0 comparing with that of Mg(HCit), Al(Cit), $Al(OH)Cit^{-}$ at all conditions;
(4) at $pH > 5$, all magnesium and aluminum ions completely form magnesium citrate complex Mg(HCit) and aluminum citrate complex $Al(OH)Cit^{-}$.

The results of Fig. 4 show for the molar ratio of the citric acid to the total molars of cations is 1:2, no magnesium citrate complex forms for all pH values, and the percentage concentration of Mg^{2+} ions is about 100%. All aluminum ions are completely in the form of the aluminum citrate complexes of Al(Cit) and $Al(OH)Cit^{-}$.

The solubility product (K_{SP}) of $Al(OH)_3$ is about 2.0×10^{-32}, however, the molar concentration of $[Al^{3+}]$ is about 6.3×10^{-17} M, 1.1×10^{-19} M, 3.4×10^{-21} M and 6.4×10^{-23} M at pH 4, pH 5, pH 6, pH 7, respectively, with $[H_3Cit]:[Mg^{2+} + Al^{3+}] = 1:1$ by our calculation, which leads to no possibility of the formation of $Al(OH)_3$ solid in present gels.

In order to achieve the complete homogeneity of magnesium and aluminum ions at atomic level in the precursor, it is very important to increase the relative concentration of magnesium and aluminum citrate complexes ((Mg(HCit), Al(Cit) and $Al(OH)Cit^{-}$)). According to the theoretical model (Figs. 1–3), at a

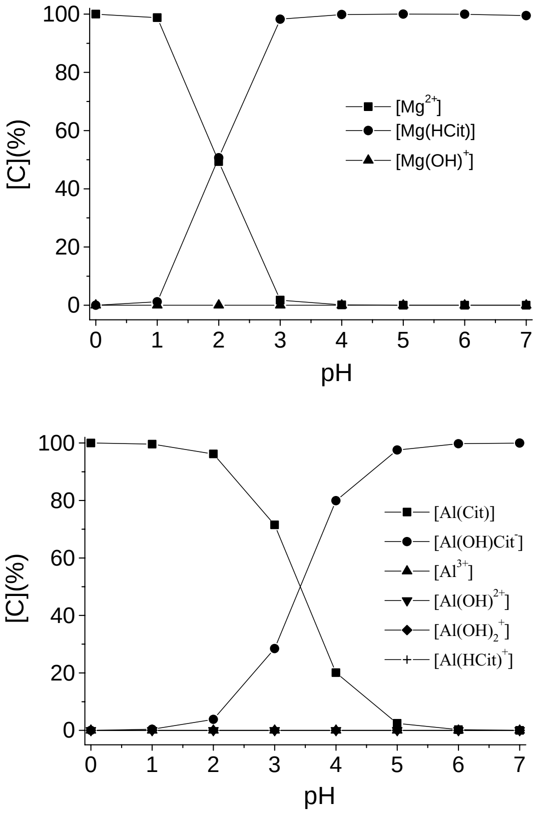


Fig. 3. The evaluated concentration of magnesium species in the solution, in which the molar ratio of citric acid to the total moles of cations is 3:1.

given concentration of citric acid, the percentage of the magnesium and aluminum citrate complex will increase to about 100% as pH increases to 5, which leads to the conclusion that the suitable process of $MgAl_2O_4$ precursor synthesis is, $[H_3Cit]:[Mg^{2+} + Al^{3+}] = 1:1$, $pH > 5$, it is also consistent with the experimental observations, i.e. the highly viscous colloid (wet gel) of $MgAl_2O_4$ precursor is easily formed at the pH value over 5 in this investigation.

The TG-DTA curves of the dry $MgAl_2O_4$ precursor with $pH = 5$ and $[H_3Cit]:[Mg^{2+} + Al^{3+}] = 1:1$ are shown in Fig. 5. The small endothermic peak about 140 °C in DTA can be assigned to the loss of free water. The weight loss thereafter can be divided into three temperature regions, namely, from 139 to 276 °C, from 276 to 577 °C, and from 577 to 820 °C, which correspond to further weight loss of about 60, 24, and 2.5%, respectively, after which there is almost no change in weight loss that can be attributed to the formation of a pure oxide system. The exothermic peak in the first temperature region (about 276.0 °C) can be contributed to the decomposition of the NH_4NO_3; the two exothermic peaks in the second temperature region at about 422.0 and 580 °C may be caused by decomposition of the citrate (Mg(HCit) and $Al(OH)Cit^-$), and the formation of $MgAl_2O_4$ spinel, respectively. The exothermic peak in the third temperature region (about 820 °C) may be arisen from the oxidation of the residue carbon.

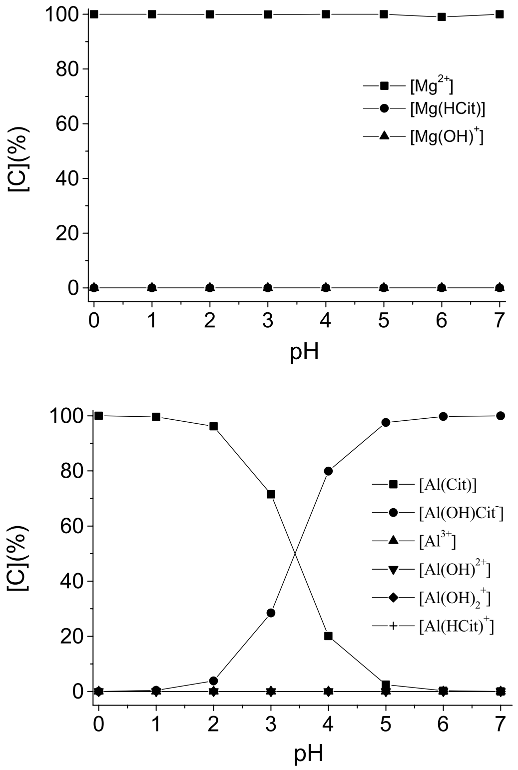


Fig. 4. The evaluated concentration of magnesium species in the solution, in which the molar ratio of citric acid to the total moles of cations is 1:2.

Fig. 6 shows the XRD patterns of the dried $MgAl_2O_4$ gels calcined at 550 °C for 5 h. The results indicate that the precursor calcined at 550 °C even for 5 h is still amorphous.

Figs. 7–9 show the XRD results of $MgAl_2O_4$ precursors fired at 600, 700 and 1000 °C, respectively. It can be seen:

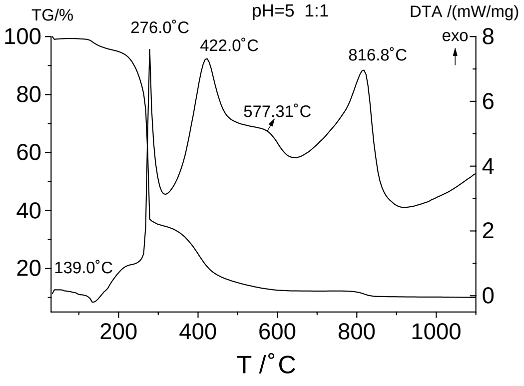


Fig. 5. Differential thermal analysis and thermogravimetric of $MgAl_2O_4$ precursor.

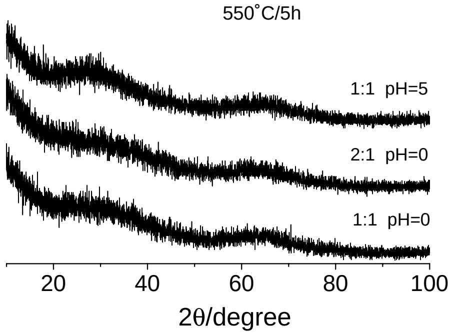


Fig. 6. XRD patterns of the $MgAl_2O_4$ precursors annealed at 550 °C for 5 h.

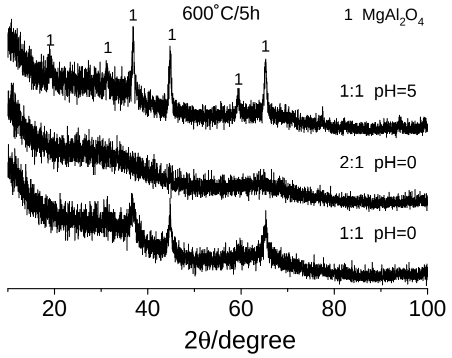


Fig. 7. XRD patterns of the $MgAl_2O_4$ precursors annealed at 600 °C for 5 h.

(1) the $MgAl_2O_4$ spinel phase began to form at 600 °C for the samples with $[H_3Cit]/[Al^{3+} + Mg^{2+}] = 1{:}1$;

(2) the temperature of $MgAl_2O_4$ spinel formation commences at about 700 °C for the samples with $[H_3Cit]/[Al^{3+} + Mg^{2+}] = 2{:}1$;

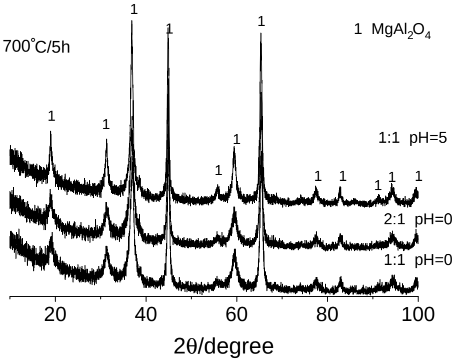


Fig. 8. XRD patterns of the $MgAl_2O_4$ precursors annealed at 700 °C for 5 h.

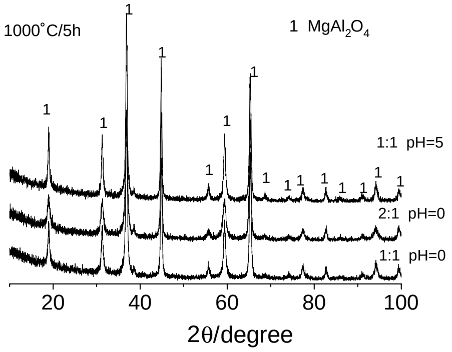
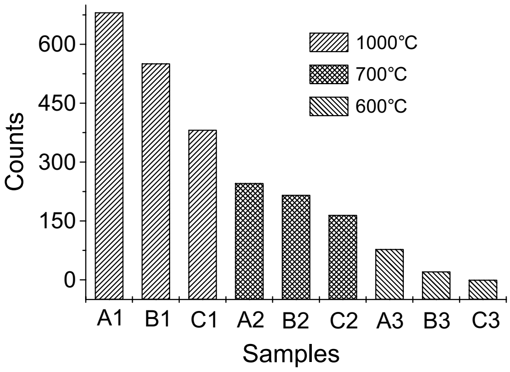


Fig. 9. XRD patterns of the MgAl$_2$O$_4$ precursors annealed at 1000 °C for 5 h.

(3) the relative content of the MgAl$_2$O$_4$ spinel of reaction product can be estimated approximately by the XRD intensity of the characteristic peaks, for specimens with [H$_3$Cit]/[Al^{3+} + Mg^{2+}] = 1:1, the XRD intensity of the three characteristic peaks (at 2θ values of 36.9, 44.8 and 65.2°, respectively) of the samples with pH = 5 are much stronger than that of the samples with pH = 0 (Figs. 7–9), this is also clearly illustrated in Fig. 10 showing the XRD intensity of the characteristic peak at 2θ values of 36.9° of specimen fired at 600, 700, and 1000 °C with different preparation conditions.

From the above results, the recommended process of ultrafine MgAl$_2$O$_4$ spinel powder synthesis is as follows: ①, pH = 5; ②, [H$_3$Cit]/[Al^{3+} + Mg^{2+}] = 1:1; ③, firing temperature: 600–700 °C.

For the Al$_2$O$_3$–MgO system, a stabilized γ-Al$_2$O$_3$–MgAl$_2$O$_4$ solid solution might form before crystallization of a pure spinel phase during heat treatment. A method has been suggested to determine whether the solid-solution was formed or not by Pasquir et al. [13], concerning the comparison of the relative intensities of the (4 0 0) and (3 1 1) peaks. A pure stoichiometric spinel should have $X = I(400)/I(311) = 0.65$ (according to JCPDS Card No. 21-1152), while $X > 0.65$ indicates a solid



(A: [H$_3$Cit]/[Al^{3+}+Mg^{2+}]=1:1, pH=5; B: [H$_3$Cit]/[Al^{3+}+Mg^{2+}]=1:1, pH=0;

C: [H$_3$Cit]/[Al^{3+}+Mg^{2+}]=2:1, pH=0;)

Fig. 10. The relative content of MgAl$_2$O$_4$ fired at different temperature.

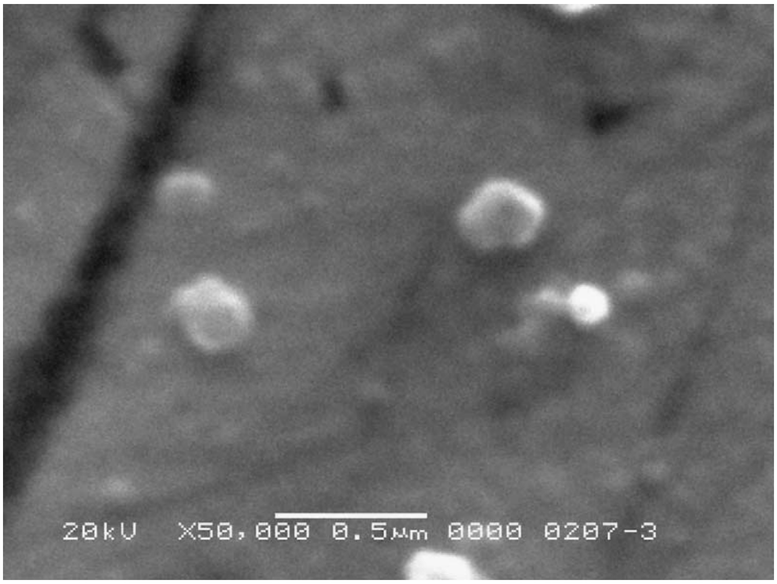


Fig. 11. SEM photograph of $MgAl_2O_4$ precursor calcined at 600 °C for 5 h (1:1, pH = 0).

solution of γ-Al_2O_3 and spinel. According to Figs. 7–9 of the present work (pH = 5), the X value at 600 °C is 0.75, indicating that γ-Al_2O_3, at least partially, was in the form of solid solution. The X value at 700 °C is 0.61, close to that of the stoichiometric spinel. On the results of Figs. 5–9, the formation process of $MgAl_2O_4$ spinel powder by citrate sol–gel can be concluded as follows: first, the decomposition of the compound of ammonia and citrate to ultrafine γ-Al_2O_3 and MgO, second, the formation of $MgAl_2O_4$ though solid-state reaction, due to the high reactivity of γ-Al_2O_3 and MgO as well as their intimate mixing, complete conversion of the precursor to spinel was achieved at a relatively low calcinations temperature of 600 °C.

Fig. 11 shows particle morphology of the precursor calcined at 600 °C for 5 h. Low-magnification revealed that the precursor contained two kinds of particles: sphercial particles of 30–50 nm in diameter and relatively spherical particles of about 200 nm in diameter. As those particles overlap, it is not possible to observe one of them individually. However, the particle size determined by X-ray diffraction is about 15 nm for the specimen fired at 600 °C ($[H_3Cit]/[Al^{3+} + Mg^{2+}] = 1:1$, pH = 0), which difference can be attributed to the clearly relatively large agglomerates formed in the product.

5. Conclusions

The calculation results of the theoretical model show that the concentrations of magnesium and aluminum citrate are the major factors affecting the citrate sol–gel process and the formation of $MgAl_2O_4$. Increasing the concentration of citric acid and pH values can increase the amount of magnesium and aluminum citrate and favor to form ultrafine $MgAl_2O_4$ powder. The theoretical model could provide valuable information and help in preparing $MgAl_2O_4$ powder using citrate sol–gel process.

The principal factors influencing ultrafine $MgAl_2O_4$ powder synthesis are: (1) Formulation: For promoting ultrafine $MgAl_2O_4$ formation at lower temperature, the optimal citric acid:metal ratio is $[H_3Cit]/[Al^{3+}+Mg^{2+}] = 1:1$. This is more effective than that of $[H_3Cit]/[Al^{3+} + Mg^{2+}] = 2:1$. (2) pH: pH = 5 is more effective than that of pH = 0 for ultrafine $MgAl_2O_4$ synthesis. (3) Temperature: The suitable firing temperature is 600–700 °C.

The formation process of $MgAl_2O_4$ spinel may have two stages. First, the decomposition of the compound of nitrate and citrate salts to γ-Al_2O_3 and MgO. Second, the solid state reaction between γ-Al_2O_3 and MgO to form $MgAl_2O_4$ spinel. $MgAl_2O_4$ spinel crystals are mostly spherical with a crystal size about 30–50 nm.

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