Low-temperature synthesis of mesoporous nanocrystalline magnesium aluminate (MgAl_2O_4) spinel with high surface area using a novel modified sol-gel method

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Abstract

A simple, template-free and scalable modified sol-gel route was developed for the synthesis of mesoporous flake-like magnesium aluminate spinel (MgAl_2O_4) at low temperature (700 °C) with high surface area (281 $\text{m}^2 \text{g}^{-1}$). The obtained spinel materials were characterized by means of physicochemical techniques including X-ray diffraction, thermogravimetric analysis, scanning electron microscopy with energy-dispersive X-ray spectroscopy, transmission electron microscopy, Fourier transform infrared spectroscopy and N_2 adsorption-desorption analysis. The propylene oxide was used as gelation and pore forming agent in the sol-gel process. Different morphologies and sizes of flake were generated by the varied synthesis conditions. The result materials reveal that the textural properties of the MgAl_2O_4 product are strongly associated with the nature and amount of additive solvent and calcination temperatures. It shows that the BET surface area decrease as the increase of calcination temperature and the optimal temperature of 700 °C result in the pure phase of MgAl_2O_4 spinel. This synthesis strategy offers a feasible

approach for scalable fabrication of mixed metal oxides for various catalytic reactions or catalyst supports due to the large surface area.

Keywords: Sol-gel; Mg-Al oxide (MgAl_2O_4); Mesoporous; Nanostructured.

Introduction

Spinel has the general formula AB_2O_4 (The valences of cations are either A^{+2} , B^{+3} or A^{+4} , B^{+2}) and with the cubic crystal system, in which the anions are located in a cubic close pack lattice and the A and B cations occupied some or all of the tetrahedral and octahedral sites in the lattice. Among the well know spinel, magnesium aluminate (MgAl_2O_4) has many industrial applications. It has many applications as catalyst support [1-5], membranes [6], sensor, dye adsorbent [7], an active component in sensors for humidity measurement [8] and an appropriate transparent ceramic based material for arc-enclosing envelops employed at high-temperature [9], due to its unique properties, such as high thermal stability (high melting point: 2135°C), unique optical properties, high mechanical strength with low expansion at high temperature, low dielectric constant, and acceptable catalytic properties. For industrial applications as an adsorbent, catalyst and catalyst support, this spinel needs high purity, small particle size, high surface area and uniform pore size distribution [1-3], which properties rely on the preparation methods. Several methods were employed for the preparation of magnesium aluminate. The solid-state [10, 11], sol-gel [12, 13], spray drying [14], pechini method [15] and co-precipitation [1, 16-18] are the most conventional methods for preparation of MgAl_2O_4 spinel. However, some of these synthesis methods are complex and expensive, which makes them difficult for large scale production. In addition, conventional synthesis methods involve high-temperature solid-state reactions, which lead to the destruction of porosity and low BET surface areas that restrict the catalytic performance of the obtained spinel materials. For this reason, it is highly desirable to create an efficient method for the controlled synthesis of a porous spinel that possesses a high BET surface area. Preparation process involving hard template or soft template is always popular since it

gives the formation of porosity and high surface area [19-25]. However, templating methods are complex, time assuming and demanding high cost which prohibits scalable production for commercialization. Among the mentioned strategies for fabrication of magnesium aluminate spinel, sol-gel has several advantages: high purity, high chemical homogeneity, low calcination temperature, etc. [26-28]. However, the metal alkoxides are often used in this method. These metal alkoxides are usually high cost and not suitable for commercially scalable production. In addition, some of them are light, moisture and heat activated, which make them unlikely for industrial applications. Hence, many attempts have been done to develop a sol-gel method based on the non-alkoxide based precursors to overcome the mentioned problems. In this case, epoxide was introduced as a gelation agent to address this concern [29, 30]. Comparing with other traditional methods, it demands less complicated process with several advantages such as low cost and temperature required for preparation of metal oxides as well as the configuration of macropores, and formation of mesopores on the surface of spinel materials. The cyclic ethers, which have much higher reactivity than their simple ethers counterparts, can be used as acid scavenger in the epoxide oxygen protonation and subsequent ring opening (Eq. 1) [31, 32].

In this sol-gel method, the aluminum nitrate and absolute ethanol can be considered as aluminum precursor and solvent, respectively. The aluminum nitrate was dissolved in ethanol to generate hydrated aluminum ion ($[\text{Al}(\text{H}_2\text{O})_6]^{3+}$) which could protonate the epoxides with its strong acidity property. Eq. 2 illustrates that the hydrated aluminum ion donates protons to propylene oxide to form the $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ species. It then produces more condensed aluminum oxide species by hydrolysis and condensation reaction (Eq. 3). The created protons can be utilized by the epoxide

during these reactions. Eq. 4 shows the irreversible opening of the ring which is happened during the nitrate ions nucleophilic attack. It results in hydrolysis of Al(III) complex by the free protons eliminated from this reaction, thus leading to the formation of a gel.

Eq. 4

In this work, a non-alkoxide sol-gel method involving propylene oxide as the gelation agent is investigated for the scalable preparation of mesoporous flake-like MgAl_2O_4 spinel with high surface area. The effects of preparation factors on the textural properties of obtained spinel materials were well studied such as the molar ratio of propylene oxide to the metal cations, the content of ethanol as solvent as well as the calcination temperature.

Experimental section

Materials

Magnesium nitrate ($\text{Mg(NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and aluminum nitrate ($\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were purchased from Sigma-Aldrich. Propylene oxide ($\text{C}_3\text{H}_6\text{O}$) and absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$) were purchased from Merck. All the chemicals were used as received. Deionized water used in all preparation process was purified.

Sample preparation

The mesoporous flak-like MgAl_2O_4 was fabricated by a modified sol-gel route. For a typical process, the desired stoichiometry of aluminum nitrate and magnesium nitrate were dissolved in a certain amount of $\text{C}_2\text{H}_5\text{OH}$ solution. After obtaining a transparent precursor solution under the

1 stirring at room temperature the propylene oxide was added. Accompanying with the consequent
2 exothermic reaction, a gel was formed after several minutes' reaction. Then the obtained gel was
3 aged at room temperature for 30 min before moving to the oven at 85 °C for drying process for
4 24h. The dried solid was calcined at a range of temperatures (600-900 °C) with a 3 °C/min ramp
5 rate and kept for 3h in air.
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8 **Characterization**

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10 X-ray diffraction (XRD) patterns of the as-prepared spinel samples were measured on a
11 PANalytical X'Pert-Pro diffractometer in a scanning range $2\theta = 10-80^\circ$. The BET (Brunauer-
12 Emmet-Teller) specific surface area and porous properties were measured via N₂ adsorption-
13 desorption at -196 °C on a BELSORP-mini II analyzer. The scanning electron microscope
14 (SEM, Nova NanoSEM 650) coupled with energy dispersive X-ray analysis (EDX) was
15 performed and transmission electron microscopic (TEM) images were obtained. The Fourier
16 transform infrared spectroscopy (FTIR) analysis was performed using an FTIR Bruker-Tensor
17 270 spectrometer.
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34 **Results and discussion**

35 **Effect of preparation conditions on crystal phase composition**

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37 The XRD patterns of the samples prepared under different preparation conditions are presented
38 in Fig. 1. The calcination temperature between 600 and 900 °C was used and the XRD patterns
39 were shown in Fig. 1a. It exhibits that the MgAl₂O₄ spinel phase cannot form until the
40 temperature reaches to 700 °C. Obviously, the crystallinity of the samples improved with the
41 increasing of calcination temperature and sharp peaks were witnessed in the samples obtained at
42 900 °C which is caused by the growth of crystal size (from 5.8 nm at 700 °C to 14.3 nm at
43 900 °C, taking facet (311) as example) as listed in Table 1. The XRD patterns can be ascribed to
44 the (111), (220), (311), (222), (400), (422), (511), (440), (530), (620) and (533) facets diffraction
45 of the standard single cubic MgAl₂O₄ spinel phase (JCPDS Card No. 77-1203) from low to high
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degree. The effect of propylene oxide on the crystal phase composition was shown in Fig. 1b. Three different molar ratio of propylene oxide with metal cations (PO/M) were used to prepare the Mg-Al spinel. All the samples show clear and sharp XRD patterns which refer to the standard MgAl_2O_4 spinel phase. However, the sample prepared with PO/M=6.5 exhibit small impurity peak at c.a. 28 degree. When the PO/M ratio increase to 11 no impurity or separated MgO and Al_2O_3 phase peaks were not observed. As the PO/M ratio reaches to 16.5, the pattern of sample suffered a drastic intensity decrease, indicating a decrease of crystal size (Table 2). By using the different amount of $\text{C}_2\text{H}_5\text{OH}$ as a solution, the crystallization degree also has been slightly affected (Fig. 1c). It is seen that the sample prepared with the ratio of $\text{C}_2\text{H}_5\text{OH}/\text{M}=25$ exhibited the highest level of crystallization with the biggest crystal size (Table 3). Increasing the $\text{C}_2\text{H}_5\text{OH}/\text{M}$ ratio inhibited the crystallization process and the growth of crystal size.

Thermal stability

Fig. 2 shows the TGA/DTA analysis of the as-obtained samples with different PO/M molar ratios. The prepared sample with PO/M molar ratio of 5.5 exhibited three weight losses in TGA curve. The first weight loss below 150 °C was related to removal of the water, including some of the hydroxyl groups and adsorbed water and also the evaporation of the remained propylene oxide in the pores, which is accompanied with a small endothermic peak in DTA curve. The sharp exothermic peak centered at 157 °C in DTA curve, which is followed by a weight loss in the region of 150–200 °C in TG curve, is assigned to combustion of $\text{C}_3\text{H}_6\text{O}$ and other compounds derived from the propylene oxide during the gelation process. In addition, the weight loss at a temperature higher than 200 °C was related to dehydration of metal hydroxides and also decomposition of nitrate groups of metal precursors. It is seen that the rapid weight loss observed at around 150 °C and also the related exothermic peak in DTA curve are sharper for the samples prepared with higher PO/M molar ratios, which is related to the higher concentration of combustible alkoxides species in these samples.

Effect of preparation conditions on surface area and pore-size distribution

The N₂ adsorption-desorption isotherms and pore-size distribution of the Mg-Al spinel samples prepared in different conditions was presented in Fig. 3. It illustrates that all the samples exhibited similar IV type isotherms, indicating the present of mesopores in the structures. The E-type adsorption loop curves as shown in the Fig. 3a, c, and e demonstrated the shape of the pores tend to be ink bottle-shape. In Fig. 3c, with the PO/M molar ratio increasing, the hysteresis loop gradually swelled up and became close to a shape of a right-angled triangle. The appearance of the triangular hysteresis loop showed that the mesopores should be in the shape of ink bottle with a small opening. It is noted that these ink bottles gradually became clear with increasing in PO/M molar ratio. In addition, the appearance of the hysteresis loop at low relative pressure (between 0.35 and 0.76) is assigned to the fine pores produced by intra-integrated pores for the sample prepared with PO/M molar ratio of 5.5. Increasing in PO/M molar ratio cause the formation region of the hysteresis loop shifting to higher relative pressure, which is due to the existence of larger pores in the samples prepared with higher PO/M molar ratio. As increasing of calcination temperature, the BET surface area of the samples was decreasing, from 305 m²·g⁻¹ at 600 °C to 52 m²·g⁻¹ at 900 °C (Table 1). In addition, the crystallite sizes were also increased by increasing in calcination temperature, which is related to crystal growth at high temperature. On the other hand, the amount of propylene oxide and C₂H₅OH has less effect on the surface area (Table 2 and 3). It is seen that there is an optimum C₂H₅OH/M ratio, in which the sample exhibited the highest BET area (Table 3). The results showed that increasing in C₂H₅OH/M ratio increased the pore volume and pore size. The crystallite sizes calculated by the Deby-Scherrer equation clearly confirmed the decrease in crystallite size with the increasing C₂H₅OH/M ratio and the optimum of the C₂H₅OH/M ratio to obtain the magnesium aluminate with the smallest crystallite size. The increase in pore volume and pore size of the samples prepared under higher C₂H₅OH/M ratios could be related to the destruction of small pores during the drying process. In the drying process, the larger mesopores are formed by filling with high boiling point liquid organic products formed during the ring opening reaction after solvent evaporation. These products can remain in

the pore of the dried gel until the temperature reaches 200 °C, and thus the larger pores are formed because of the surface tension. The results confirmed that increasing in C₂H₅OH/M ratio caused the pore size distribution shifting to larger sizes. As propylene oxide can act as a phase separation inducer, the increase in PO/M molar ratio enhances the phase separation tendency. This leads to the formation of larger mesopores with the relatively weak skeleton. The prepared structure undergoes to collapse and shrink after drying and calcination steps, which causes the destruction of the wall of mesopores and formation of larger mesopores. Furthermore, the increase in PO/M molar ratio effectively shortens the necessary time for gelation. The pore size shifts to bigger values with an increase in PO/M (Fig. 3d). This is due to this fact that the propylene oxide can accelerate the increase in pH value and decrease in the timing of the sol-gel transition parallel to the phase separation. This can fix the transient structure with small major size in the early stage of phase-separating. Propylene oxide in this method acts as a gelation agent and also serves as a pore forming agent in the preparation of magnesium aluminate. As shown in Fig. 3b, d, and f, all the samples exhibited single modal pore size distributions.

Effect of preparation conditions on morphology

The SEM images of the Mg-Al spinel samples calcined at different temperatures and EDX mapping of sample calcined at 700 °C are shown in Fig. 4 and 5. It is observed that all the samples displayed mesoporous flake-like architecture (Fig. 4). The porosity of the structure decreased while the flake size increased as the rise of calcining temperature from 600 to 900 °C. The magnesium aluminate calcined at 900 °C showed the lowest porosity due to sintering of particles at high temperature.

R. Jiang et al. [33] also reported the same results on the effects of calcination temperature on the textural properties of the mesoporous titania spheres prepared by modified sol-gel method using chitosan/poly(vinyl alcohol) hydrogel beads as a template. They showed that the BET area and pore volume decreased with the increase of calcination temperature.

EDX mapping analysis (Fig. 5) of the sample prepared with a certain condition (PO/M=11, C₂H₅OH/M=40 at 700 °C) confirmed the present of Al, Mg, and O elements and well dispersion of each chemical elements. The element spectra in Fig. 5f contained a high peak of Al and two equal peaks of Mg and O. Pt is from the coating process before the SEM analysis to improve the conductivity of each sample. Fig. 6 shows the TEM images of MgAl₂O₄ sample calcined at 700 °C, PO/M=11, C₂H₅OH/M=40. It clearly exhibits the flake-like structure with the diameter size ranged in 10-14 nm. Mesoporous architecture is visible. In addition, the high magnification TEM image (Fig. 6d) presents the exposed facets (440), (311) and (111) which are corresponding to the XRD diffraction results.

FTIR analysis

Fig. 7 present the FTIR profiles of the samples without calcination with MgO/Al₂O₃ molar ratio of 1 and calcined sample at 700 °C. The observed peaks in the region 3400 cm⁻¹ and peak at 1640 cm⁻¹ related to the OH bending vibration and broad H-O-H stretching of adsorbed water, respectively. The strong absorption band at 1380 cm⁻¹ can be referred to the presence of NO₃⁻ characteristic vibration. Besides, the broad adsorption bands centered at 650 cm⁻¹ can be related to the Al-O stretching frequency in tetra and octahedrally coordinated metal ions. [34] The peak located at 2400 cm⁻¹ is recognized as the absorbance stretching of CO₂ molecules. The bands at 2400 and 2420 cm⁻¹ are attributed to the CH₃CH₂ vibration, which disappeared after calcination. The absorption bands at 2920 and 2841 cm⁻¹ were assignable to the asymmetric and symmetric stretching vibrations of CH₃ bonds in alkyl chains, respectively. The sample prepared with PO/M=11 show the best adsorption ability of water and CO₂ on the surface of material, indicating the largest available surface area and surface adsorption property. It is seen that the intensity of adsorbed water peak decreased after calcination while the intensity of CO₂

adsorption peak remained. This result demonstrates that the CO₂ may chemisorb on the surface.

The peak of nitrate groups almost disappeared after calcination due to the thermal decomposition.

Conclusions

In summary, high-surface-area magnesium aluminate spinel with mesoporous flake-like monocrySTALLine structure was successfully prepared via a simple and scalable sol-gel method at low temperature. It is found that, by this synthesis strategy, the calcination temperature at 700 °C can form the cubic MgAl₂O₄ spinel phase without any separate impurity phase of MgO and Al₂O₃. The prepared spinel calcined at 700 °C exhibited a high surface area of 264 m²·g⁻¹ with a small pore size about 6.6 nm. It also shows that the textural properties and morphologies can be significantly affected by the nature and amount of propylene oxide as gelation and pore forming agent and ethanol as a solution. An optimal preparation condition with the proper amount of the propylene oxide and ethanol has been investigated to obtain the spinel samples with the highest BET surface area. Such a mesoporous flake-like spinel can be idea catalyst or metal support for the heterogeneous catalysis application due to the high surface area and scalable production.

Acknowledgments

This work was supported by Iran National Science Foundation (INSF) and the University of Kashan by Grant No. 158426/95. The provided supports are gratefully acknowledged.

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Captions for Figures and Tables

Table 1. Textural properties of the sample calcined at different temperature of PO/M=11 and C₂H₅OH/M=40.

Table 2. Effect of the PO/M molar ratios on the textural properties of the calcined samples at 700 °C and C₂H₅OH/M=40.

Table 3. Effect of C₂H₅OH/M molar ratio on the textural properties of the calcined samples at 700 °C and PO/M=11.

Fig. 1. (a) XRD patterns of the sample calcined at different temperature, PO/M=11, C₂H₅OH/M=40, (b) the samples prepared with different PO/M molar ratios and calcined at 700 °C, C₂H₅OH/M=40 and (c) the samples prepared with different C₂H₅OH/M molar ratios and calcined at 700 °C, PO/M=11.

Fig. 2. TGA/DTA analysis of the as-prepared samples prepared with different PO/M molar ratios and calcined at 700 °C, C₂H₅OH/M=40.

Fig. 3. (a) N₂ adsorption/desorption isotherms and (b) Pore size distributions of the samples calcined at different temperatures, PO/M=11, C₂H₅OH/M=40. (c) N₂ adsorption/desorption isotherms and (d) Pore size distributions of the samples prepared with different PO/M molar ratios, C₂H₅OH/M=40 and calcination temperature= 700 °C (e) N₂ adsorption/desorption isotherms and (f) Pore size distributions of the samples prepared with different C₂H₅OH/M molar ratios and calcined at 700 °C, PO/M=11.

Fig. 4. SEM images of the samples calcined at different temperatures, a) 600 °C, b) 700 °C. c) 800 °C and d) 900 °C of the PO/M=11, C₂H₅OH/M=40.

Fig. 5. The corresponding EDS elemental mapping images (a–e) and EDX spectrum (f) of the MgAl₂O₄ sample calcined at 700 °C, PO/M=11, C₂H₅OH/M=40.

Fig. 6. TEM images of the MgAl₂O₄ sample calcined at 700 °C, PO/M=11, C₂H₅OH/M=40.

Fig. 7 FTIR spectra of the calcined samples at 700 °C with PO/M=11, C₂H₅OH/M=40 and the as-prepared samples without calcination prepared with different PO/M ratio with C₂H₅OH/M=40.

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Table 1. Textural properties of the sample calcined at different temperature of PO/M=11 and C₂H₅OH/M=40.

Calcination temperature (°C)	BET (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Crystallite size (nm)		
				(311)	(400)	(440)
600	305	0.529	6.23	-	-	-
700	264	0.436	6.61	5.8	7.1	5.9
800	111	0.460	16.46	9.9	11.4	11.5
900	52	0.248	18.81	14.3	17.4	17.9

Table 2. Effect of the PO/M molar ratios on the textural properties of the calcined samples at 700 °C and C₂H₅OH/M=40.

PO/M	BET (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Crystallite size (nm)		
				(311)	(400)	(440)
5.5	277	0.369	5.32	5.9	8.3	7.1
11	264	0.436	6.61	5.8	7.1	5.9
16.5	281	0.449	6.38	3.4	6.4	5.2

Table 3. Effect of C₂H₅OH/M molar ratio on the textural properties of the calcined samples at 700 °C and PO/M=11.

C ₂ H ₅ OH/M	BET (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Crystallite size (nm)		
				(311)	(400)	(440)
25	232	0.372	6.38	6.6	8.1	10.1
40	264	0.436	6.61	5.8	7.1	5.9
55	249	0.463	7.42	6.8	7.9	6.7

Fig. 1. (a) XRD patterns of the sample calcined at different temperature, PO/M=11, C₂H₅OH/M=40, (b) the samples prepared with different PO/M molar ratios and calcined at 700 °C, C₂H₅OH/M=40, and (c) the samples prepared with different C₂H₅OH/M molar ratios and calcined at 700 °C, PO/M=11.

Fig. 2. TGA/DTA analysis of the as-prepared samples prepared with different PO/M molar ratios and calcined at 700 °C, $C_2H_5OH/M=40$.

Fig. 3. (a) N₂ adsorption/desorption isotherms and (b) Pore size distributions of the samples calcined at different temperatures, PO/M=11, C₂H₅OH/M=40, (c) N₂ adsorption/desorption isotherms and (d) Pore size distributions of the samples prepared with different PO/M molar ratios, C₂H₅OH/M=40 and calcination temperature= 700 °C, (e) N₂ adsorption/desorption isotherms and (f) Pore size distributions of the samples prepared with different C₂H₅OH/M molar ratios and calcined at 700 °C, PO/M=11.

Fig. 4. SEM images of the samples calcined at different temperatures, a) 600 °C, b) 700 °C, c) 800 °C, and d) 900 °C of the PO/M=11, C₂H₅OH/M=40.

Fig. 5. The corresponding EDS elemental mapping images (a–e) and EDX spectrum (f) of the MgAl_2O_4 sample calcined at 700 $^\circ\text{C}$, PO/M=11, $\text{C}_2\text{H}_5\text{OH}/\text{M}=40$.

Fig. 6. TEM images of the MgAl_2O_4 sample calcined at 700 $^\circ\text{C}$, PO/M=11, $\text{C}_2\text{H}_5\text{OH}/\text{M}=40$.

Fig. 7 FTIR spectra of the calcined samples at 700 °C with PO/M=11, C₂H₅OH/M=40 and the as-prepared samples without calcination prepared with different PO/M ratio with C₂H₅OH/M=40.

Graphical Abstract