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Low temperature synthesis of nanocrystalline magnesium aluminate spinel by a soft chemical method

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Abstract

A new simple soft chemical method – synthesizing nanocrystalline $MgAl_2O_4$ spinel powder with oxalic acid as organic template and nitric acid as an oxidizing agent – is described. The method was developed with the objective of obtaining phase pure nanocrystalline $MgAl_2O_4$ spinel powder with uniform particle size and morphology at a much lower temperature than that used by conventional methods. The synthesized powders were characterized by X-ray diffractometry (XRD), thermogravimetry (TGA), Fourier transform infrared spectroscopy (FTIR), surface area analysis (BET) and field emission scanning electron microscopy (FE-SEM). The average crystallite size of the single phase material was 30 nm. Through this method, porous $MgAl_2O_4$ powder with a high surface area of 162.2 m^2g^{-1} and 141 m^2g^{-1} was obtained at 600 °C and 700 °C, respectively.

Keywords: A. Solution evaporation; B. Oxalic acid; C. Spinel; D. Nanopowder

1. Introduction

Spinels are any class of minerals of general formulation AB_2O_4 which crystalize in the cubic crystal system, with the oxide anions arranged in a cubic close pack lattice and the cations 'A' and 'B' occupying some or all of the octahedral and tetrahedral sites in the lattice. Magnesium aluminate, $MgAl_2O_4$, a binary oxide with a spinel structure, has a lot of important properties for wide applications. The high melting point (2135 °C), good mechanical strength at high temperatures, excellent chemical inertness, low dielectric constant, good catalytic properties and good thermal shock resistance confer to the use of $MgAl_2O_4$ in the metallurgical, electrochemical, radio technical and chemical industrial fields [1–3]. Its excellent stability under radiation makes it an attractive material for optical transmission applications in the visible and IR portion of the spectrum as transparent ceramics [4]. A relatively new application of $MgAl_2O_4$ is in the field of catalyst where it can be used as support for metallic catalysts due to its low acidity, hydrophobic character, high thermal resistance, chemical inertness and compatibility with the metallic phase [5–8].

The preparation of $MgAl_2O_4$ with high purity and chemical homogeneity, low particle size and uniform size distribution depends mainly on synthesis methods. Magnesium aluminate powder has been prepared by many techniques such as solid state [9,10], co-precipitation [11], sol–gel [12,13], spray drying [14], freeze-drying [15], and combustion synthesis [16]. However, some of these processes are either complex or expensive which limits their large scale production. Other disadvantages include the requirement of high temperature, inhomogeneity, lack of stoichiometry and low surface area of the product. In general, high surface area is associated with smaller particle sizes for different catalytic and noncatalytic applications. Hence, low temperature soft chemical synthesis of nanosized magnesium aluminate particles has ample scope for application in the above-mentioned different fields.

In this study we report a new method for synthesis of $MgAl_2O_4$ nanoparticles by an organic acid template route. Oxalic acid is used here as a complexing agent and HNO_3 as an oxidizing agent. The synthesized powders were characterized

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by TGA, FTIR, XRD, FESEM and BET surface area analysis.

2. Experimental

Magnesium aluminate nanopowder was synthesized by a solution evaporation route. 0.01 M magnesium nitrate hexahydrate (99.5% Merck) and 0.02 M aluminum nitrate nonahydrate (99.5% Merck), dissolved in 2 N nitric acid, were mixed together in a beaker.

Oxalic acid dihydrate (0.06 M) was then added to the solution under constant stirring. This resultant solution was then heated on a hot plate under continuous stirring condition to its boiling temperature until all the liquid was evaporated out of the solution. There was an immense evolution of brown fumes toward the end of the reaction leaving a white mass at the base of the beaker. These fine powders were dried on a hot plate at 130 °C for 30 min. The green samples prepared were calcined at different temperatures to get phase pure material.

The powders were characterized by X-ray diffraction (Phillips PW 1710) using CuKα radiation. The powder morphology was studied using FESEM (supra 45 vp). Thermogravimetric analysis (TGA) was carried out with NETZSCH 409C analyzer, FTIR of the powders were taken by Nicolet Model 5PC FTIR. BET surface area analyses were carried out with Quantachrome instruments NOVA4000e.

3. Result and discussion

Fig. 1 shows the X-ray diffraction analysis of the synthesized powder heated in air at different temperatures. The synthesized powder (green powder) is of amorphous nature. After heat treatment $MgAl_2O_4$ phase begins to form. As the calcination temperature increases, the peaks become sharper and the formation of crystalline phase pure magnesium aluminate is completed at a temperature as low as 700 °C. All of the diffraction peaks can be perfectly indexed to cubic spinel-structured $MgAl_2O_4$ (JCPDS Card no. 77-1203). Nevertheless, calcinations at temperatures above 700 °C promote the formation of a more crystalline spinelic phase, as observed through the gradual increase in the peak intensities accompanied by sharpening of the peaks. The average crystallite size (30 nm) of the powders was calculated using Debye Scherrer's equation.

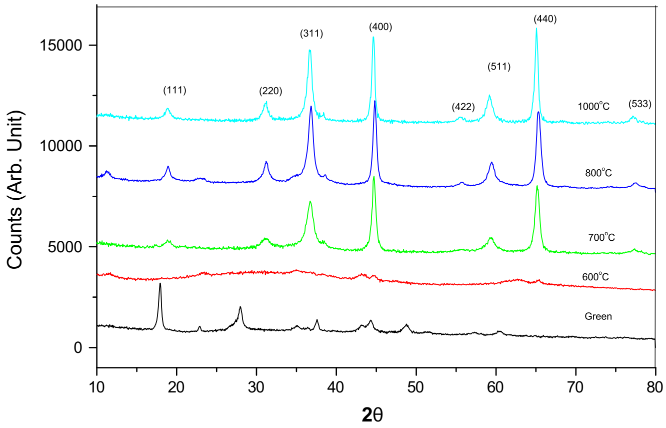

Fig. 1. XRD of the magnesium aluminate precursor and its calined forms at different temperatures: (a) Green precursor, (b) calcined at 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C and (f) 1000 °C.

Fig. 2 shows a TGA curve of the uncalcined powder up to 1000 °C at a heating rate of 10 °C/min. The TGA graph shows a steady loss in weight up to 420 °C (about 60%) which is due to the presence of trapped nitrates, residual carboxylate, unburned carbon and entrapped water (as also confirmed by IR dip in Fig. 3). A slight loss in weight is observed from 600 °C to 800 °C ($<5\%$) which may be due to the presence of occluded water.

The FTIR spectra (400–4000 cm^{-1}) for green and calcined (at different temperatures) powders are shown in Fig. 3. The IR spectrum of the green synthesized powder shows a broad band around 3414 cm^{-1} due to ν (O–H) of the lattice water molecule [17]. Broad band around 1690 cm^{-1} corresponds to

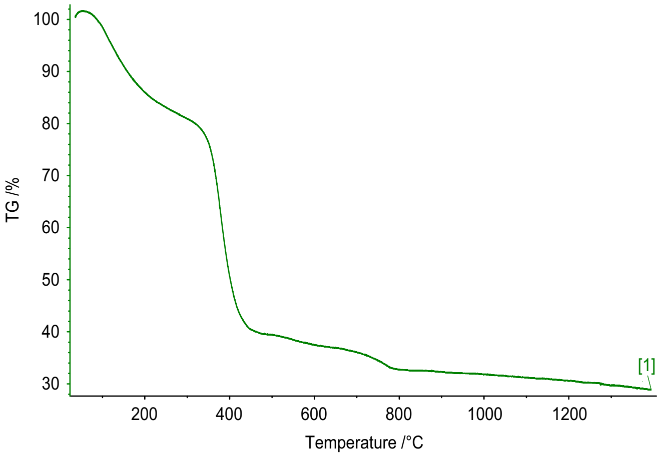

Fig. 2. TGA curve of the magnesium aluminate precursor.

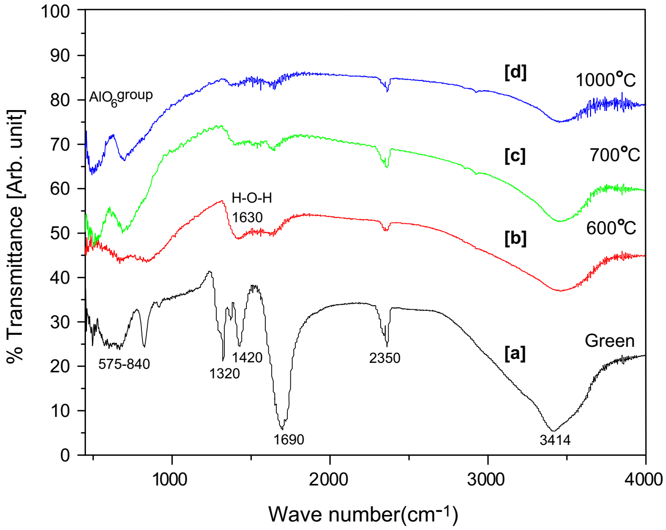

Fig. 3. FTIR spectrum of magnesium aluminate precursor and its calcined forms at different temperatures; (a) precursor, (b) calcined at 600 °C, (c) 700 °C and (d) 1000 °C.

the ν_{asym} (C═O) of coordinated oxalate. The bands in the zone of 1320–1420 cm^{-1} is attributed to ν_{sym} (C═O) of coordinated oxalate which is overlapped with intense nitrate peak at 1380 cm^{-1} [18]. The peak at 2350 cm^{-1} of the IR spectrum is due to ambient CO_2. The band at 1630 cm^{-1} is due to the bending mode of H–O–H vibration [17]. The peaks in the range 575–840 cm^{-1} are difficult to predict. But here broad bands around 692 and 515 cm^{-1} become stronger with increase in calcination temperature corresponding to AlO_6 group which build up $MgAl_2O_4$ spinel and leads to the formation of $MgAl_2O_4$ spinel [19]. As the calcination temperature increases, the peaks due to O–H, C–O, C–H and nitrates gradually disappear indicating the removal of organic constituents and nitrate residues. Although XRD shows formation of phase pure $MgAl_2O_4$ at 700 °C, FTIR studies show the presence of slight impurities due to the presence of occluded water. This might be the result of inter absorption due to packing of powder with KBr.

The FESEM micrograph of powder calcined at 700 °C is shown in Fig. 4. Loosely aggregated extremely fine particles are observed. The image of nonagglomerated particles is given in inset. The crystallite size is in agreement with that obtained from XRD studies (30 nm).

Fig. 5 shows adsorption desorption isotherms of synthesized magnesium aluminate calcined at 600 °C and 700 °C. The isotherm of sample calcined at 600 °C shows the characteristics of nonporous or macro-porous solids and include in type II compound of IUPAC classification while calcined at 700 °C shows the trend of pore size reduction and a transition from type II to type V compound. Consequently surface area reduces from 162.2 m^2g^{-1} to 141 m^2g^{-1} when calcination temperature increases from 600 °C to 700 °C. Synthesis of magnesium aluminate by ceramic, mechano-chemical and co-precipitation method, calcined at 900 and 800 °C shows specific surface area values of 37, 117 and 108 m^2g^{-1} respectively [5]. The surface area reported through metal chitosan complexation route is 168.3 m^2g^{-1} calcined at 700 °C [20]. In comparison to others our method produces high specific surface area magnesium aluminate spinel nanopowder by a simple economic procedure. High surface area and highly porous structure of the synthesized magnesium aluminate finds potential application as catalyst or catalytic support.

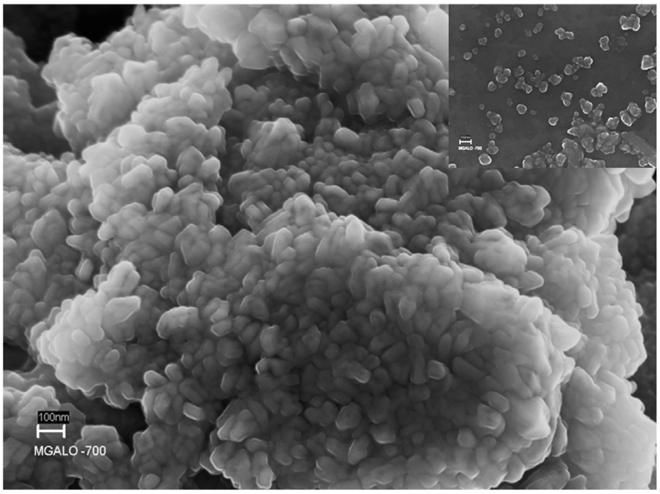

Fig. 4. FESEM micrographs of agglomerated magnesium aluminate powder calcined at 700 °C and its nonagglomerated image (inset).

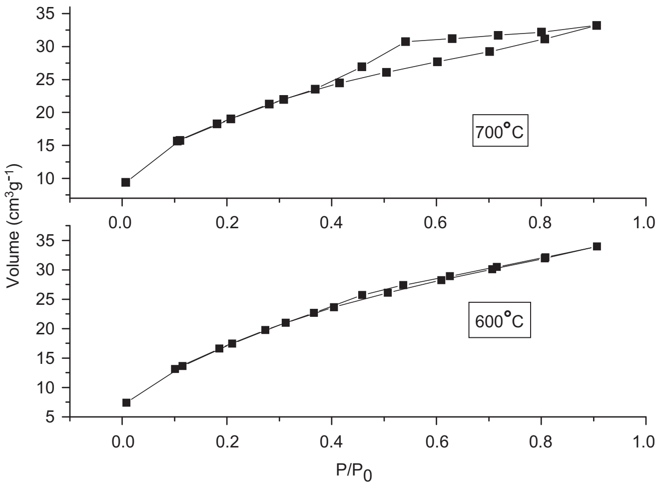

Fig. 5. N_2 adsorption/desorption isotherms of samples calcined at 600 °C and 700 °C, respectively.

The uniqueness of oxalic acid as a chelating agent in synthesizing magnesium aluminate probably resides in the formation of transition metal aluminooxalate precursor, $Mg_3[Al(OX)_3]_2$ as stated in the synthesis of ferrites by thermolysis of ferrioxalate precursors [21]. In the present case, the aluminooxalate complex undergoes in situ decomposition which occurs toward the end of the reaction when HNO_3 becomes concentrated enough to oxidize the complex giving rise to the product. That is the reason we could see only residual carboxylates attached to the metal atom in the IR spectra. The formation of magnesium aluminate was favored due to the close proximity of the reacting metal atoms in the precursor which on decomposition in the presence of nitric acid resulted in active local heteroatomic units giving rise to the reaction product.

4. Conclusion

The present study describes a simple low temperature synthesis route for preparing $MgAl_2O_4$ nanopowders through a solution evaporation method. Compared to the conventional solid-state reaction process and co-precipitation method, $MgAl_2O_4$ phase can be formed at a much lower temperature through aluminooxalate precursor method. The synthesized material showed the formation of a spinel phase, with an initial crystallization temperature of 700 °C, having a high specific surface area and porosity. This indicates that the methodology involved the oxidation of aluminooxalate precursor by HNO_3 accompanied by the evolution of various gases (such as CO_2, NO_2 and water vapor) and the gas evolution helped the product to obtain a fine grain structure. This preparation led to the obtainment of materials with important properties for application in catalytic processes with high values for surface area and pores. Oxalic acid and nitric acid present in the solution play a key role for the synthesis of $MgAl_2O_4$ at a low temperature.

Acknowledgment

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