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Synthesis of Nano Crystalline $MgAl_2O_4$ Spinel Powder by Microwave Assisted Combustion

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Abstract: Stoichiometric $MgAl_2O_4$ spinel nanoparticles were synthesized by microwave assisted combustion reaction from aluminium nitrate nanohydrate ($Al(NO_3)_3·9H_2O$) and Sol-Gel prepared magnesium hydroxide ($Mg(OH)_2$) in the presence of urea ($(NH_2)_2CO$) as a fuel, in about 20 min of irradiation. X-ray diffraction (XRD) studies reveal that microwave assisted combustion synthesis route yields single-phase spinel nanoparticles with larger crystalline size (around 75 nm) than other conventional heating methods. Scanning electronic microscope (SEM) images show nanoparticles with spherical shape and homogenous morphology. The surface area measurements (S_{BET}) show crystals with 2.11 m^2/g and 0.0033 mL/g pore volume.

Key words: $MgAl_2O_4$ nanoparticles; spinel; microwave assisted reaction

The magnesium aluminate with spinel structure offers an attractive combination of properties such as high mechanical strength at high temperature, high melting point (2135℃), high chemical inertness and thermal stability[1-3]. Due to these properties, it is greatly desired as a refractory material[4], humidity sensor[5], catalyst or catalyst support and recently as an excellent transparent ceramic material for high temperature arc-enclosing envelopes and alkali-metal vapor discharge devices[6]. Nowadays this spinel has owned many applications in metallurgical, chemical, electro technical, catalysis, electronic and glass industries[7-8].

Over the last few decades various novel techniques have been applied for the synthesis of $MgAl_2O_4$ spinel including Sol-Gel[9], spray drying[10], freeze-drying[11], mechanical activation[12], organic gel-assisted citrate process[13]. Although wet-chemical techniques have successfully been used for the preparation of pure spinel nanoparticles at relatively low temperatures, but have not received much commercial attention because of the expensive row materials and multiple processing steps[14-17]. The conventional preparation method of $MgAl_2O_4$ spinel is to calcine the mixture of metal oxides at elevated temperatures (1625℃ for 2 h), which has disadvantages of large aggregates and inhomogeneous compositions[18-19]. Recent works show combustion synthesis for preparation of binary oxides has many advantages including homogeneity, high purity, formation of crystalline oxide powders in shorter time periods and lower amount of external energy[20-23].

In our previous work, the coprecipitation and combustion methods were applied to prepare $MgAl_2O_4$ spinel particles with conventional heating[24]. In this paper, application of microwave-assisted combustion synthesis technique for preparation of $MgAl_2O_4$ spinel has been reported and physical properties of the synthesized powders are compared with that of prepared by conventional heating method.

1 Experimental procedure

1.1 Powder synthesis

Analytical grade aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$), magnesium chloride hexahydrate ($MgCl_2.6H_2O$) and urea (CH_4N_2O) were purchased from Merck (99%) and were used without further purification. A solid mixture containing aluminum nitrate and Sol-Gel synthesized magnesium hydroxide[25] with $n(Al^{3+})/n(Mg^{2+})$= 1:2 and urea with n(urea)/n(metal) = 5:3 was taken in a pyrex glass dish and after complete mixing was irradiated with microwaves in a domestic microwave oven (National, 1000W, input range 210–230V-ac SOHZ, microwave frequency 2.45GHz).

1.2 Characterization

Phase analysis of the samples was carried out by X-ray diffraction (XRD; Bruker's D8 advance system, Bruker's AXS, GmbH, Germany) using CuKα radiation. The crys-

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tallite size of $MgAl_2O_4$ spinel was estimated with the aid of Debye-Scherrer equation (L_{hkl}=K$\lambda/\beta_{hkl}\cos\theta$, where K is a constant taken as 1 and β_{hkl} is the integral breadth that depends on the width of the particular (*hkl*) plane, λ = 0.15406 nm, the wavelength of the CuKα source, and θ is the Bragg's angle) using the XRD data of the spinel (311) reflection[26]. A Micromerities analyzer (Gemini 2375 V4/02 Instrument 1D:1) was used for Brunauer-Emmett-Teller (BET) surface area measurements. The BET surface area was measured by nitrogen physisorption at liquid nitrogen temperature −196℃. Prior to measurements, the samples were evacuated (up to 0.133 Pa) at 180℃ for 2 h. A PHILIPS XL-30 scanning electron microscope (SEM) was used to observe the particle morphology of the synthesized and ground spinel powders.

2 Results and discussion

Nanoparticles of magnesium aluminate formed by endothermic redox reaction during a microwave assisted combustion method. The combustion reaction can be expressed as follow:

$2Al(NO_3)_3{\cdot}9H_2O + Mg(OH)_2 + 5CH_4N_2O \rightarrow MgAl_2O_4 + 13N_2 + 5CO_2 + 29\ H_2O$

Aluminum nitrate is an oxidizer and urea is a fuel[20-21, 27]. Oxidation valences of the Al, Mg, C, N, O, and H are +3, +2, +4, 0, −2 and +1, respectively[28-30]. Therefore, the total oxidizing and the reducing valences of aluminum nitrate, magnesium hydroxide, and urea become −15, 0 and +6, respectively. In order to obtain maximum energy for the spinel formation reaction, and also balance the total oxidizing and reducing valances in the mixture, the stoichiometric mole ratio (2:1) of the $Al(NO_3)_3{\cdot}9H_2O$ (total valence −15) and $Mg(OH)_2$ (total valence 0) and 5 mole urea are required (2(−15) + 1(0) + n(+6) = 0 or n = 5).

The net enthalpy (ΔH, 25℃) of the reaction was calculated from the standard enthalpy of formation (ΔH_f, 25℃) of products and reactants using the following thermodynamic data: $Al(NO_3)_3{\cdot}9H_2O$: −897.38 kcal/mol; $Mg(OH)_2$: −924.5kcal/mol; CH_4N_2O: 79.7kcal/mol; $MgAl_2O_4$: −547.38 kcal/mol; N_2: 0 kcal/mol; CO_2: −94.05kcal/mol; H_2O: −57.79 kcal/mol[31-32]. According to these thermodynamic data the combustion reaction is endothermic ($\Delta H°$ = 425.77 kcal/mol, 25℃).

Within 5 min of irradiation, reaction mixture was converted into a clear solution and started to boil. After about 20 min of irradiation, the concentrated mixture solution burst into flames and resulted into a foamy white powder. X-ray diffraction pattern of synthesized powder is shown in Fig. 1. This pattern shows that prepared powders are well crystallized with single-phase spinel structure[33]. Table 1 shows the particle size, BET surface area and pore volume of microwave assisted synthesized $MgAl_2O_4$ spinel nanoparticles. The size of particles calculated from XRD peaks by using Scherrer's formula and the (311) plane was considered for the crystallite size calculation (around 75 nm)[26]. For the purpose of comparison, physical properties of magnesium aluminate spinel nanoparticles which were produced by recent various methods, *i.e.* conventional solid state[34], co-precipitation[24], conventional combustion[24], and microwave-assisted solid-state[14] routes, are listeded in Table 1. Although applying microwave irradiation results in formation of spinel powders with larger crystallite size, smaller BET surface area and pore volume than other traditional methods, it reduces the duration of whole preparation process. In the conventional solid-state methods metal oxide powders must be milled, granulated, dry-pressed in the form of pellets and sintered at 1625℃ for at least 2h[34-35]. Furthermore, most times mineralizer[36], additives like ZnO[37] or sintering aids as $AlCl_3$[7, 38] are required. Applying coprecipitation and also conventional combustion methods are also require sintering

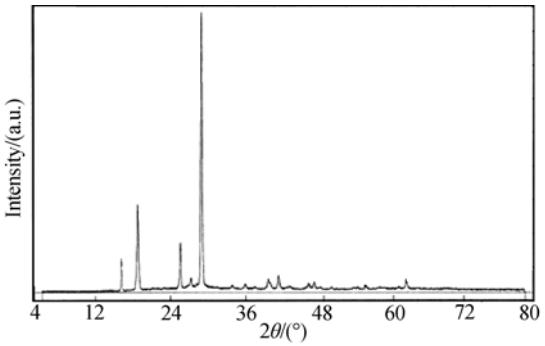

Fig. 1 X-ray diffraction pattern of $MgAl_2O_4$ spinel nanoparticles

Table 1 Physical properties of $MgAl_2O_4$ spinel nanoparticles produced by the various methods

Methods	BET surface area /($m^2{\cdot}g^{-1}$)	Crystallite size[a] /nm	Pore volume /($mL{\cdot}g^{-1}$)	References
Microwave combustion	2.1	75	0.0033	This work
Conventional solid state	8.1	44	–	[34]
Coprecipitation	8.1	15	0.0313	[24]
Conventional combustion	28.2	27	0.0436	[24]
Microwave solid state	36.0	66	–	[14]

[a] $MgAl_2O_4$ crystallite size is calculated from (311) plane[26]

at high temperatures, *i.e.* 1000℃ for 2 h[24, 39]. In microwave assisted solid-state method carbon black has been added to metal oxides as a microwave susceptor up to 50wt% (after activation at 550℃ for 6 h) and also SiC are used as a bottom plate. These precursors must be irradiated by microwave for 60 min in order to magnesium aluminate spinel to form[14]. According to Ganesh *et al.*, a solid mixture of metal nitrates and urea as a fuel will produce the nanoparticles of spinel in 45 min microwave irradiation[40]. It seems that replacing magnesium nitrate by active magnesium hydroxide decreased the irradiation time for more than 55% in this work.

It is well known that heating mechanism in microwave processing is fundamentally different from conventional processing. Microwave radiation is absorbed and converted rapidly to thermal energy from inside the material and therefore a dramatic decrease of processing time and energy consummation will result[41]. Therefore, by applying microwave irradiation and replacing active magnesium hydroxide as a precursor instead of magnesium oxide or nitrate in this combustion method, the time duration for preparation of spinel nanopowders is decreased and electrical heating and sintering process is omitted. This method can be regarded as an effective and economic method for preparation of spinel due to its convenient process, simple experimental setup, significant time and energy saving and high purity products. Therefore, this method should be considered as an alternative route for the fabrication of $MgAl_2O_4$ nanopowder.

Generally, increasing temperature treatment due to the sintering process increases the crystallite sizes of powders[42-45]. Therefore, it can be concluded that microwave assisted combustion synthesized spinel powders are exposed to higher temperatures than conventional heating prepared powders. According to the SEM image (Fig. 2) microwave-assisted combustion synthesized sample has spherical shape with homogenous morphology.

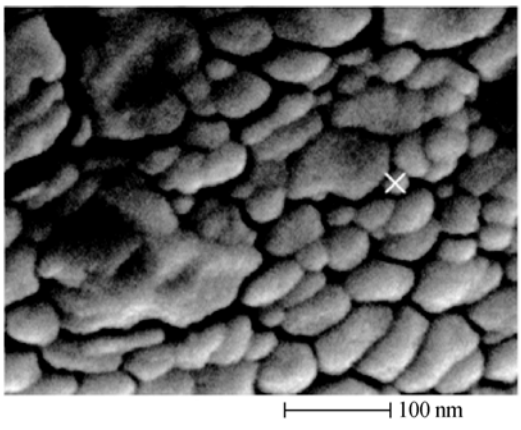

Fig. 2 SEM image of $MgAl_2O_4$

3 Conclusion

$MgAl_2O_4$ spinel nanoparticles can be prepared by microwave-assisted combustion method and applying synthesized magnesium hydroxide as a reagent in 20 min. Spinel nanoparticles synthesized through this method are exposed to higher temperatures than conventional heating methods and have larger crystallite size (around 75 nm). This method is technically simple, cost effective and time- and energy-saving compared with conventional heating methods.

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