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The effect of synthesis conditions on the physicochemical properties of magnesium aluminate materials

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ABSTRACT

Magnesium aluminate-based materials were prepared by applying different methods: (*i*) mechanochemical milling of the initial mixture of magnesium and aluminium nitrate powders (in appropriate stoichiometric amounts) followed by heat treatment at temperatures of 650 °C and 850 °C and (*ii*) melting of the mixture of nitrate precursors at 240 °C followed by thermal treatment at 650 °C, 750 °C and 850 °C. The effect of synthesis method on the structure and morphology of the obtained solids was studied by using various techniques such as: nitrogen adsorption-desorption isotherms, powder XRD, IR spectroscopy and SEM. It was shown that the mechanochemical milling performed before calcination procedure leads to obtaining of nanocrystalline magnesium aluminate spinel phase at lower temperature of 650 °C in comparison with the method using thermal treatment only (at 750 °C). The obtained nanomaterials exhibit mesoporous structure.

1. Introduction

Nanostructured materials of an average crystalline size of a few nanometers have been of a great interest in the last decades. These materials exhibit increased strength, hardness and specific heat, as well as improved ductility and reduced density and elastic modulus, etc. The magnesium aluminate spinel ($MgAl_2O_4$) is one of the well-known and widely used material. Its solid-state synthesis from magnesia and alumina is revealed by inter-diffusion of cations ($3Mg^{2+} \Leftrightarrow 2Al^{3+}$) through the product layer between the oxide particles at high temperatures (> 1400 °C) [1]. It possesses fcc structure of oxygen ions with eight molecules per unit cell, in which there are 64 tetrahedral and 32 octahedral sites [2]. The aluminium ions occupy the 16 octahedral sites and the magnesium ions – eight tetrahedral sites in the ideal case [2]. This ceramic material has been found application in the chemistry, metallurgy and electrochemistry because of its refractory properties, good thermal shock resistance and mechanic resistance, high melting point (2135 °C), high chemical inertia, low thermal expansion coefficient, low density and excellent optical and dielectric properties [3,4]. Many researchers have been synthesized the magnesium aluminate by various synthesis methods, for example, such as self-heat-sustained (SHS) technique [5], surfactant assisted precipitation [6], autoignition technique [7], a wet-chemical process [8], co-precipitation [9,10], molten-salt method [11], reactive sintering using bauxite and magnesite [12], nitrate–citrate combustion route [13], sol–gel auto combustion method [14], microwave-assisted combustion synthesis [15], co-crystallizing and decomposing of aluminium and magnesium nitrates mixture [2,16], etc. Among the methods for obtaining of nanostructured materials, mechanochemical process is very popular due to its simplicity and low process cost. Synthesis method by mechanochemical activation is an effective way to improve the interaction and contact of the reactants by milling process, which leads to enhancement of the chemical homogeneity of product and to decrease of the severity of thermal treatment [17]. The mechanochemical milling can accelerate the reaction in a multi-component system by significantly decrease of the temperatures of thermal treatment [18]. Many researchers have been used various mechanochemical synthesis methods at different conditions for obtaining magnesium aluminate spinel [1,2,18–25]. Different precursors have been used for obtaining of nanocrystalline magnesium aluminate spinel by mechanochemical activation followed by annealing such as Al_2O_3 and $NgCO_3$ [1,18,19] or $MgCl_2$ and $AlCl_3$ in the presence of NaO together with a small amount of water [20], etc.

Due to the high chemical inertness in the acidic and basic environments, as well as, due to the high thermal resistance at elevated temperatures, the magnesium aluminate spinel has been found wide application in heterogeneous catalysis as carrier of different supported metal oxide catalysts for clean energy production and environmental production. It was shown that $MgAl_2O_4$ obtained by co-precipitation of the solutions of the Al and Mg precursor salts, followed by calcination at high temperatures, leads to obtaining of materials with a high surface area suitable as supports for catalysts [26–29].

In the present paper, it was attempted to synthesize magnesium

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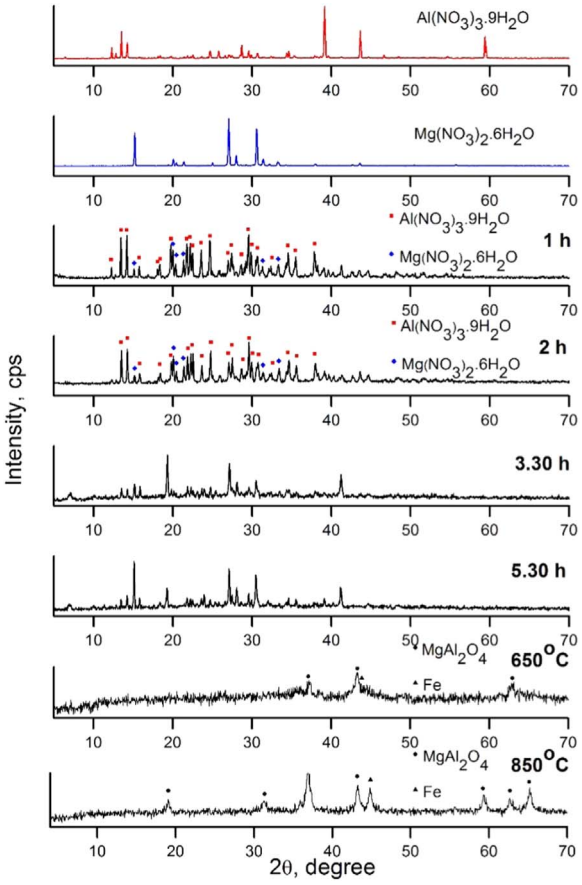

Fig. 1. Powder X-ray diffractograms of magnesium aluminate samples obtained by Method 1.

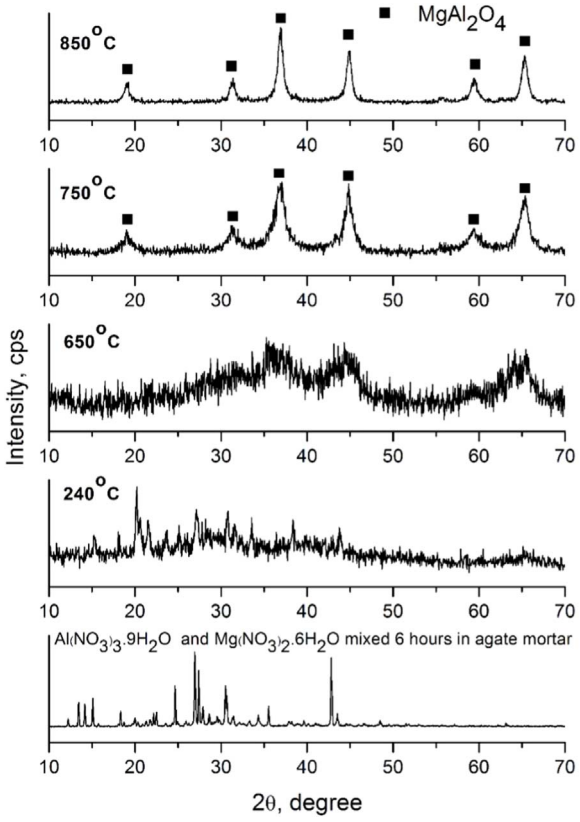

Fig. 2. Powder X-ray diffractograms of magnesium aluminate samples obtained by Method 2.

aluminate by different methods and to study the effect of synthesis method on the physicochemical properties of the obtained spinel materials. It was studied the influence of the prior segregation of the phase selection and the evolution in thermally decomposed samples synthesized from nitrate precursors. For this purpose, the magnesium aluminate was prepared by mechanochemical treatment for various periods or by melting of the mixture of the salts of magnesium and aluminium nitrates in appropriate amounts with subsequent annealing. The powder X-ray diffraction analysis (PXRD), infrared spectroscopy (IR), scanning electron microscopy (SEM) and N_2 adsorption-desorption isotherms were performed in order to characterize the synthesized samples.

2. Materials and methods

2.1. Sample preparation

Magnesium aluminate samples were prepared by two different synthesis methods. The first method labeled as Method 1 was used mechanochemical milling of the initial mixture of powders precursors of $Al(NO_3)_3{\cdot}9H_2O$ (99% purity, Merck) and $Mg(NO_3)_2{\cdot}6H_2O$ (99% purity, Merck) in an appropriate stoichiometric amount of 2:1, followed by heat treatment procedure at 650 °C and 850 °C in air. The samples were milled at different times of 1 h, 2 h, 3.30 h and 5.30 h using a high-energy ball milling by planetary ball mill type PM 100, Retsch, Germany. The mechanochemical milling process was performed in air atmosphere at room temperature in a stainless steel milling container of 250 ml and with a rotation speed 390 rpm. The mass ratio between balls and powder was 17:1.

The second preparation method denoted as Method 2 was a mixing of initial materials of magnesium and aluminium nitrates powders (in a molar ratio of 1:2) in agate mortar for 6 h followed by thermal treatment at 240 °C in air for 4 h to obtain a melt. After that, the sample powder was annealed at different temperatures of 650 °C, 750 °C and 850 °C in air for 2 h at each temperature.

2.2. Characterization

The powder XRD patterns were recorded on a Bruker D2 Phaser diffractometer within the range of 2θ values between 4° and 75° using Cu K_α radiation (λ = 0.154056 nm) at 40 kV (step size of 0.05° and time per step of 1 s). The phases were identified using of JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997).

Infrared spectra of the magnesium aluminate samples were performed on a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) in KBr pellet (0.5% studied substance). The spectra were collected in the middle IR region (400–4000 cm^{-1}) using 50 scans at a resolution of 4 cm^{-1} (data spacing 1.928 cm^{-1}).

The SEM investigations were carried out by the scanning electron microscope JSM-5510 at acceleration voltage of 10 kV and different magnifications of 10,000 and 20,000. The samples were prepared by dispersing the powders in acetone. Ultrasonic oscillation for 1 h was

Table 1
Calculated values of average crystallite size (D), lattice strain (ε) and unite cell parameter (a) of the magnesium aluminate phase.

Sample	D (nm)	ε × 10^{-3} (a.u.)	A (Å)
$MgAl_2O_4$-650-Method 1	8.3	3.5	8.11
$MgAl_2O_4$-850-Method 1	12.5	2.1	8.09
$MgAl_2O_4$-750-Method 2	7.6	3.6	8.07
$MgAl_2O_4$-850-Method 2	15.0	3.4	8.08