



Article Structural, Optical, and Catalytic Properties of MgCr₂O₄ Spinel-Type Nanostructures Synthesized by Sol–Gel Auto-Combustion Method

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Abstract: Spinel chromite nanoparticles are prospective candidates for a variety of applications from catalysis to depollution. In this work, we used a sol–gel auto-combustion method to synthesize spinel-type MgCr₂O₄ nanoparticles by using fructose (FS), tartaric acid (TA), and hexamethylenetetramine (HMTA) as chelating/fuel agents. The optimal temperature treatment for the formation of impurity-free MgCr₂O₄ nanostructures was found to range from 500 to 750 °C. Fourier transform infrared (FTIR) spectroscopy was used to determine the lattice vibrations of the corresponding chemical bonds from octahedral and tetrahedral positions, and the optical band gap was calculated from UV–VIS spectrophotometry. The stabilization of the spinel phase was proved by X-ray diffraction (XRD) and energy-dispersive X-ray (EDX) analysis. From field-emission scanning electron microscopy (FE-SEM), we found that the size of the constituent particles ranged from 10 to 40 nm. The catalytic activity of the as-prepared MgCr₂O₄ nanocrystals synthesized by using tartaric acid as a chelating/fuel agent was tested on the decomposition of hydrogen peroxide. In particular, we found that the nature of the chelating/fuel agent as well as the energy released during the auto-combustion played an important role on the structural, optical, and catalytic properties of MgCr₂O₄ nanoparticles obtained by this synthetic route.

 ${\it Keywords:}\ MgCr_2O_4\ nanoparticles;\ sol-gel\ auto-combustion\ method;\ spinel;\ catalysis$

1. Introduction

Spinel-type oxides, with the general formula AB_2O_4 (where A is divalent metal and B is trivalent metal), are some of the most technologically important materials, having



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). played a key role in the development of modern electronics [1], in nuclear technology as a radiation-resistant materials [2], etc. In particular, the magnesiochromite MgCr₂O₄ possesses magnetic, electrical, and optical properties that make it the leading candidate for numerous technological applications in catalysis [3–5], high-temperature ceramics [6], interconnecting materials for solid oxide fuel cells [7], multifunctional ceramic sensor [8], and sensing [9–11].

As such, the development of reproducible synthetic methodologies for the reliable fabrication of spinel-type nanomaterials with controllable physical and chemical properties is of prime scientific and technological importance. Thus, various methods have been proposed to synthesize $MgCr_2O_4$ nanostructures, including the hydrothermal route [12], microwave [13], mechanical activation [14], high-temperature solid-state reaction [6], coprecipitation [3], and spray pyrolysis [15]. These methods have some drawbacks, such as high cost, lower specific surface area, large size distribution, and/or lower catalytic activity of the resulting nanoparticles. A valuable alternative is the sol-gel auto-combustion synthesis [16–18] as an easy and cheap method for forming high-quality nanoparticles. According to this method, MgCr₂O₄ nanoparticles are synthesized via a multi-step procedure including the dissolution of stoichiometric amounts of metal precursors and the chelating/fuel agent into an appropriate solvent, the formation of a gel, followed by the gradual increase of the reaction temperature and initiation of auto-combustion, during which the main chemical reactions occur, followed by the final calcination step. This synthetic method for the fabrication of spinel nanostructures allows for the growth of the nanoparticles with predictable properties. However, a proper selection of the chelating/fuel agent, metal precursors, and reaction conditions are oftentimes crucial to the purity and morphological characteristics of the final product that, in turn, will strongly influence the electrical, catalytic, magnetic, and optical properties of these spinel nanoparticles.

The main focus of the present paper was the exploration of the optimum parameters of the chelating/fuel agents in order to obtain MgCr₂O₄ nanoparticles with a pure spinel structure. In particular, we investigated the influence of the combustion agent on the structural formation, nanoparticle morphology, and catalytic characteristics. Moreover, it was found that the morphology of MgCr₂O₄ nanoparticles can be predicted from the combustion agent properties.

Several studies have been devoted to the investigation of the influence of the chelating/fuel agent on the properties of spinel-type compounds synthesized by a sol–gel autocombustion approach. In particular, Slatineanu et al. [19] have shown that citric acid, tartaric acid, glycine, and egg white could be considered good candidates for chelating/fuel agents yielding single phase Zn ferrite nanoparticles at a calcination temperature of 973 K. The authors concluded that the nature of the fuel affects the duration of the autocombustion reaction, yielding nanoparticles with an average size of about 40–50 nm [19].

Another interesting study was reported by Hu et al. [20], who performed a comparative analysis of MgCr₂O₄ and CoCr₂O₄ chrome-containing spinels. They used glucose as a complexing agent in the sol-gel method, followed by a post-synthesis calcination of the samples in air at 1400 °C. This procedure yielded MCr₂O₄ (M = Mg, Co) particles with a polyhedron morphology and average sizes ranging from around 0.4 to 3 μ m. The auto combustion approach has been also used for the synthesis of the well-studied MgAl₂O₄ spinel nanoparticles. For example, Saberi et al. [21] used citric acid and ammonia solution in order to produce magnesium aluminate nanoparticles with a size between 20 and 100 nm by thermal treatment under argon atmosphere for 1 h at 700 °C and one hour more at 900 °C, respectively. In another paper, Habibi et al. [22] studied the influence of the calcination temperature on the sample morphology obtained within the sol-gel route by using propylene oxide as a fuel agent. Interestingly, the obtained MgAl₂O₄ nanoparticles has flake-like shapes, which meant that the combustion agent and the condition of synthesis allowed for variation in the particle morphology and properties. These preliminary studies shed some light on the formation of spinel nanoparticles by the combustion sol–gel method. However, the influence of the fuel/combustion agent on the morphology of $MgCr_2O_4$

nanoparticles synthesized by using hexamethylenetetramine, fructose, and tartaric acid is still not fully understood.

2. Results and Discussion

In order for the variation in size of the synthesized spinel nanoparticles to be explained, the enthalpy of combustion of the solid chelating/fuel agents should be considered. Under standard conditions, the values of the enthalpy of combustion $\Delta_c H^\circ$ of the combustion agents in solid state are -1159 ± 0.3 kJ/mol for tartaric acid [23], -2810.4 ± 0.3 kJ/mol for fructose [24], and -4200.11 ± 0.6 kJ/mol for hexamethylenetetramine [25]. Interestingly, the electron microscopy data showed that the average size of the nanoparticles increased with increasing enthalpy value of combustion of the fuel agent (see ESI). On the basis of these experimental observations, we hypothesized that chelating/fuel agents with a combustion temperature under 500 °C, short burning time of the gel, and a value of the enthalpy of combustion of about -1000 kJ/mol promote the formation of cuboidal nanoparticles with an average size of 10–16 nm similar to those of the TA chromite sample. Likewise, fuel agents with combustion temperatures above 1000 °C, longer burning time of the gel, and with values of the enthalpy of combustion around the -4000 kJ/mol will yield nanoparticles larger than 20 nm in size, whereas fuel agents with intermediate values of the combustion time, burning time, and enthalpy of combustion yield spinel nanoparticles with an average size ranging between 15 and 20 nm.

2.1. Infrared Spectroscopy

The three series of nanoparticles were analyzed using Fourier transform infrared (FTIR) spectroscopy in order to confirm the formation of the metal–oxygen bonds and ensure the elimination of the organic and nitrogen phases during the post-synthesis annealing process. Figure 1 shows the IR spectra recorded on the three series of samples synthesized by using HMTA, FS, and TA as chelating/fuel agents after thermal treatment at various temperatures: 500 °C, 700 °C, 750 °C, and 900 °C. The vibrational bands recorded at 638 cm⁻¹, 640 cm⁻¹, and 640 cm⁻¹ on the three samples correspond to the lattice vibrations of the Cr³⁺–O^{2–} from the tetrahedral positions. The markers recorded at 492 cm⁻¹, 498 cm⁻¹, 496 cm⁻¹, 418 cm⁻¹, 410 cm⁻¹, and 415 cm⁻¹ were attributed to the lattice vibration bands recorded at about 940–950 cm⁻¹ were attributed to the presence of Cr(VI)-O bond vibrations [26]. The absorption bands recorded around 1630 cm⁻¹ (scissors-bending of H₂O) indicate adsorption of water during the cooling of the samples and hydrophilic nature of the obtained particles [27].



Figure 1. FTIR spectra recorded at ambient temperature after annealing the samples at 500 °C (**a**), 700 °C (**b**), 750 °C (**c**), and 900 °C (**d**).

The absence of the bands associated with the Cr(VI)-O bond vibrations suggests that the spinel form of MgCr₂O₄_HMTA nanoparticles were already formed after the thermal treatment at 500 °C, which confirmed the reduction of Cr (VI) to Cr (III) [26]. However, for the other two samples, the Cr(VI)-O bands disappeared only after the thermal treatment at 750 °C. Figure 1a–d shows the FTIR spectra recorded at various annealing temperatures on the three samples.

2.2. Phase Analysis

Powder X-ray diffraction analysis was carried out for samples that had been annealed at 750 °C. Figure 2 shows the XRD patterns collected for the spinel chromite samples synthesized in the presence of hexamethylenetetramine, fructose, and tartaric acid. The diffractograms clearly indicate the formation of pure MgCr₂O₄ spinel structures, all the peaks being successfully assigned to reflections of the MgCr₂O₄ reference patterns [28]. Moreover, no other reflections ascribable to crystalline MgO, Cr₂O₃, and CrO₃ phases were detected.



Figure 2. XRD diffractograms of (**a**) MgCr₂O₄_HMTA, (**b**) MgCr₂O₄_FS, (**c**) MgCr₂O₄_TA, and (**d**) reference spectra of MgCr₂O₄ recorded with Diamond 4 software.

Determination of the crystallite size for the three $MgCr_2O_4$ samples obtained from different precursors was performed by using the Williamson–Hall method [29]. As such, the crystallite size and microstrain are related to the size broadening through the following relationship:

$$\beta_{hkl}cos\theta = \frac{K\lambda}{D} + 4\varepsilon sin\theta \tag{1}$$

where β_{hkl} represents the full width at half maximum (FWHM) value of the diffraction peak, *K* is the shape factor (0.94), λ is the wavelength of Cu K α (1.5406 Å) radiation, *D* is the crystalline size, and ε is the integral breadth related to the microstrain. Therefore, by plotting the variation of the $\beta_{hkl} \cos\theta$ vs. $4\sin\theta$, we were able to calculate the crystalline size and the lattice microstrain of the samples from the intercept with the *y*-axis and slope of the line, respectively. Figure 3 shows the peak fitting of the five most intense peaks and the Williamson–Hall plots of the MgCr₂O₄_HMTA sample. The peak fitting was performed with Origin Pro software by using a Gaussian function.



Figure 3. Peak fitting by using a Gaussian function (**a**) and Williamson–Hall plot (**b**) for the $MgCr_2O_4$ _HMTA sample.

The calculated values of the crystallite size (K) and microstrain (ε) for the MgCr₂O₄_HMTA, MgCr₂O₄_TA, and MgCr₂O₄_FS samples were found to be K = 13.5 ± 0.1; 18.7 ± 0.3, 20.1 ± 0.3 nm; and ε = -2.15%, 3.27%, and 0.65%, respectively. Interestingly, the lattice microstrain in the MgCr₂O₄_HMTA sample was found to be negative, indicating that the crystal was under a slight compressive stress, whereas for the MgCr₂O₄_TA and MgCr₂O₄_FS samples, the crystal was under a slight tensile stress. The values of the crystallite size in all three samples were consistently smaller than the values of the particle size determined by SEM analysis, thereby indicating that the MgCr₂O₄ nanoparticles presented a multidomain structure with respect to the scattering of X-rays.

2.3. UV–VIS Analysis

The UV–VIS absorption spectra were collected to determine the optical band gap values of the samples. In order to do this, the Tauc method was applied [30]:

$$(\alpha h\nu) = A(h\nu - E_g)^n, \tag{2}$$

where α is the absorption coefficient; *h* is the Planck's constant; *v* is the frequency of incident lights; *A* is an arbitrary constant; *E*_g is the optical energy band gap; and *n* is the exponent that characterizes the type of optical transition, i.e., n = 1/2 for direct transition and n = 2 for indirect transition. Figure 4 presents $(\alpha hv)^2$ (where n = 1/2) as a function of *hv*. The energy gap values were obtained at the intersection of the fitted linear part above the sharp absorptions around 3 eV with the horizontal axis of energy. The *E*_g values obtained for MgCr₂O₄_HMTA, MgCr₂O₄_FS, and MgCr₂O₄_TA were around 2.80 eV, 2.87 eV, and 2.98 eV, respectively. The acquired optical spectra presented a weak absorption with a shoulder of around 2.5 eV. This absorption peak might be attributed to the oxygen vacancies defects, similarly to that reported on the well-studied MgAl₂O₄ spinel [31,32].



Figure 4. Direct Tauc plot transition for $MgCr_2O_4$ nanoparticles synthesized by hexamethylenetetramine (HMTA) (1), fructose (FS) (2), and tartaric acid (TA) (3).

2.4. Morphological Analysis

Field-emission scanning electron microscopy (FE-SEM) analysis indicates that, regardless of the precursor used as a fuel, the resulting spinel-type nanopowders are relatively homogeneous and consist of uniformly sized nanoparticles (Figure 5). The average size of the nanoparticles were around 22 nm, 19 nm, and 16 nm for MgCr₂O₄_HMTA, MgCr₂O₄_FS, and MgCr₂O₄_TA, respectively (see Figures S1 and S2 from ESI).



Figure 5. FE-SEM micrographs recorded on (a) $MgCr_2O_4$ _HMTA, (b) $MgCr_2O_4$ _FS, and (c) $MgCr_2O_4$ _TA.

The EDX analysis of $MgCr_2O_4$ _HMTA nanoparticles further confirmed the formation of $MgCr_2O_4$ (Figure S3a). The amount of carbon detected was around 2% and most likely corresponded to the carbon-coated copper grid on which the spinel chromite nanoparticles were deposited prior to the elemental analysis.

These differences in size were presumably related to the thermal energy released during the auto-combustion process. Since the flame temperature in the case of HMTA was about 1100 °C [16], it led to the release of a larger amount of energy compared with the synthesis of MgCr₂O₄_FS and MgCr₂O₄_TA, whereby the flame temperatures were about 425 °C and 505 °C, respectively, and therefore less thermal energy was released for the respective equimolar quantity of chelating/fuel agents. The larger size of MgCr₂O₄_FS nanoparticles than that of MgCr₂O₄_TA could be explained by taking into account the burning time of the fuel agent, i.e., fructose had a burning time of about 3 min since the second one had a burning time of only 5 s. The size effect was also observed in both electrical and dielectric properties (see Figure S4 from ESI). As expected, the MgCr₂O₄_HMTA nanoparticles, characterized by a higher diameter, were the most conductive and had the highest value of the dielectric permittivity among the three samples (around 21 at 1 Hz). On the other hand, the MgCr₂O₄_TA particles, which had the smallest diameter, were less conductive and had a dielectric constant of around 10 at 1Hz.

2.5. Catalytic Activity

Figure 6 shows the catalytic activity of the three series of MgCr₂O₄ nanoparticles, whereby it can be seen that the catalytic activity of MgCr₂O₄_TA was substantially higher than that of the MgCr₂O₄_HMTA and MgCr₂O₄_FS, whose catalytic activity towards the decomposition of H_2O_2 was almost negligible.



Figure 6. Catalytic activity of MgCr₂O₄ nanoparticles on the reaction of hydrogen peroxide decomposition.

As the catalytic activity is usually affected by the specific surface (size and shape) as well as by the crystalline structure of the catalyst, the higher activity of the MgCr₂O₄_TA nanoparticles could be tentatively attributed to the higher specific surface of the nanoparticles since the three series had the same crystal structure, according to the XRD analysis. These experimental results strongly suggest that the catalytic activity of the MgCr₂O₄ nanoparticles on the decomposition of hydrogen peroxide sharply increased when their average size decreased below 16 nm. Additionally, as revealed by EDX analysis, the MgCr₂O₄_TA nanoparticles presented a higher amount of chromium on their surface, which can be also considered responsible for their increased catalytic activity (Figure S2c). Taking this into consideration, we can tentatively explain the mechanism of catalytic action by a radicalic mechanism:

$$Cr^{3+} + 3HO-OH = Cr^{6+} + 3HO^{-} + 3HO + 3e^{-}$$
 (3)

$$Cr^{6+} + 3e^{-} + 3HO-OH = Cr^{3+} + 3H^{+} + 3HOO$$
 (4)

$$HOO \cdot + HO^* = O_2 + H_2O \tag{5}$$

$$HO + *OH = 1/2 O_2 + H_2O$$
 (6)

$$H^+ + HO^- = H_2O \tag{7}$$

Such a mechanism involved the oxidation of the Cr^{3+} ions and the generation of HO radicals followed by its subsequent reduction to Cr^{3+} and the combination of the radicalic species with formation of H₂O and molecular oxygen, respectively.

3. Materials and Methods

3.1. Synthesis of MgCr₂O₄ Nanoparticles

Analytical-grade $Mg(NO_3)_2 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were used as metal precursors, whereas hexamethylenetetramine (HMTA), fructose (FS), and tartaric acid (TA) were used as chelating and combustion agents, respectively. The molar ratio of the metal cations was Mg^{2+} : Cr^{3+} 1:2, whereas the molar ratio of chromite: chelating/fuel agents was 1:3.

Each synthesis was performed by mixing the reagents into the respective stoichiometric ratio followed by their dissolution in distilled water. The resulting dark violet reaction mixture was kept under air and stirred at 75 °C until a gel was formed. The gel mixture was subsequently placed in a sand bath for thermal treatment. The heating step consisted of bringing the reaction mixture to 100 °C, and then it was heated up to 350 °C with an increased temperature step of 50 °C. For each temperature steps, the gel mixture was annealed for 1 h. In order to obtain a single-phase spinel-type structure, all the asprepared samples were subjected to an additional heat treatment at 500 °C, 700 °C, 750 °C, and 900 °C for 5, 7, 8, and 9 h, respectively. The optimization of the reaction conditions was performed by analyzing the samples after each synthesis. A schematic diagram of MgCr₂O₄ nanoparticle synthesis is presented in Figure 7.



Figure 7. Schematic diagram of the synthetic route for the fabrication of MgCr₂O₄ nanoparticles.

3.2. Nanoparticle Characterization

To monitor the formation of the spinel structure and the absence of organic phases, we used FTIR spectroscopy. The room temperature IR spectra were collected using a PerkinElmer Spectrum TwoTM spectrometer (PerkinElmer, Waltham, MA, USA) in attenuated total reflectance (ATR) mode. The X-ray powder diffractograms (XRD) were recorded using a Bruker D8 Advance diffractometer (Brucker, Billerica, MA, USA) equipped with a Cu anode ($\lambda = 0.15406$ nm). Scanning electron microscopy images and elemental analysis were carried out with a Hitachi SU-70 Field Emission Scanning Electron Microscope (Hitachi, Tokyo, Japan) equipped with an Oxford Instrument EDX-detector. The UV–VIS spectra were recorded using an OceanOptics USB2000 spectrophotometer (OceanOptics, Tampa, FL, USA) and colloidal solutions of nanoparticles suspended in water in the presence of citric acid. The dielectric analysis was performed using a CONCEPT 40 Broadband Dielectric Spectrometer (Novocontrol GmbH, Montabaur, Germany) equipped with an Alpha-A high-performance frequency analyzer in a frequency range from 0.1 Hz to 1 MHz.

3.3. Study of the Catalytic Properties of MgCr₂O₄ Nanopowders

The catalytic properties of the MgCr₂O₄ nanoparticles were studied by measuring the volume of the formed oxygen during the catalytic decomposition of hydrogen peroxide. In a typical experiment, 100 mg of catalyst was added to 15 mL of 16% NaOH solution. The analyses were conducted on the setup for gas volume measurements (see the schematic representation in the Figure S5 from ESI). After 10 min of stirring the mixture containing MgCr₂O₄ nanoparticles and the alkaline solution, a volume of 1.5 mL of 3% H₂O₂ solution was injected, and the amount of released oxygen was recorded in time.

4. Conclusions

In this study, hexamethylenetetramine, fructose, and tartaric acid were used for the first time as chelating/fuel agents for the rational synthesis of spinel MgCr₂O₄ nanoparticles by using a combustion sol–gel method. The reaction conditions were optimized to ensure the versatility and reliability of the proposed route, and the resulting optimal protocol for pure spinel phase formation is reported. The experimental results strongly suggest that several factors, including the burning time of gel, the combustion temperature, and the enthalpy of combustion of the solid chelating/fuel agents, influence the size, electric properties, and dielectric properties of the resulting spinel nanoparticles. Catalytic activity of these nanoparticles for the decomposition of hydrogen peroxide decomposition showed that the maximum catalytic activity occurred when the size of the nanoparticles was smaller than 16 nm, presumably the result of an increasing amount of chromium on the surface of the nanoparticles.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3 390/catal11121476/s1, Figure S1: Measured average size of MgCr2O4_HMTA—(a), MgCr2O4_FS—(b) and, MgCr2O4_TA—(c) nanoparticles; Figure S2: Set of SEM images used to determine the size histograms; Figure S3: EDX elemental analysis of MgCr2O4 nanoparticles synthesized by hexamethylenetetramine (HMTA)—(a), fructose (FS)—(b) and tartaric acid (TA)—(c); Figure S4: Frequency dependence of the real part of the AC electrical conductivity (a) and of the real part of dielectric permittivity (b) recorded at room temperature, on the three series of spinel MgCr2O4 nanoparticles; Figure S5: Schematic representation of experimental setup used in the evaluation of the catalytic properties; Table S1: Average particle size and size distribution of MgCr₂O₄ nanoparticles synthesized by hexamethylenetetramine, tartaric acid and fructose.

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