Microwave combustion and magnetic properties of spinel Zn-CoAl₂O₄ nanoparticles

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Abstract

Spinel Zn-CoAl₂O₄ (x = 0.0 and 0.5) nanoparticles were synthesized using urea assisted microwave-assisted combustion method. The absence of surfactant/catalysts has led to a simple, cheap and fast method of synthesis of spinel nanoparticles. The as-synthesized spinel nanoparticles were characterized by XRD, FT-IR spectroscopy, HR-SEM, HR-TEM, EDX, and vibrating sample magnetometer. The formation of spinel nanoparticles was confirmed by HR-SEM and HR-TEM and their possible formation mechanisms were also proposed. Powder XRD, FT-IR, SAED and EDX results confirmed the formation of pure and single cubic phase CoAl₂O₄ with well-defined crystalline. VSM measurements revealed that Zn-doped CoAl₂O₄ samples have weak ferromagnetic behavior and the magnetization values decreases with increasing the concentration of Zn²⁺ ions in the CoAl₂O₄ lattice.

Keywords: Spinel aluminate; Nanoparticles; Magnetic properties.

1. Introduction

Spinel nanocrystalline materials are classes of binary transition metal oxides signify an attractive in the past decade, due to their small size exhibits novel physical and chemical properties leads to a various potential applications [1-10]. Recently, nanostructured materials signify an attractive in nanoscience and nanotechnology, duo to novel physical, electrical,

optical, magnetic and catalytic property than that of bulk materials [11,12]. Among various transition metal oxides, CoAl₂O₄, has gained lot of attention in multidisciplinary areas, due to their efficiency in ceramics, electronic, optical, catalyst, catalyst supports, aerospace, paints, dielectrics and sensing applications [13-16]. CoAl₂O₄ offers many favorable properties such as mechanical strength, thermal stability, and low temperature sintering ability, high chemical stability, wide band-gap energy, excellent optical transparency and good metal dispersion capacity [17, 18]. Spinel CoAl₂O₄ is largely used in paints for coloration, ceramics, enamels, paper, plastics, rubber and fibers [19].

A variety of methods have been used for the preparation of spinel CoAl₂O₄ nanostructures such as low-temperature, such as sol-gel, hydrolysis, and polymerized complex methods [20-23]. However, the above conventional methods desirable costly equipments, materials and laborious synthetic procedures, thus leading to the tedious polluting process. Recently, a novel and facile method has been used to prepare nanomaterials with high surface area, called microwave combustion method (MCM). In this MCM approach the samples are prepared at low temperatures, low cost with good control of size, structure and morphology, due to its fast reaction kinetics, cleanliness and efficiency [24,25]. Also, MCM route of preparation is easy, fast and low energy with soft method than the above said methods [26-28]. Furthermore, to our knowledge, no literature is available on the synthesis, structural, opto-magnetic and catalytic properties of Zn-doped CoAl₂O₄ nanostructures by a simple MCM route.

Moreover, spinel Zn-CoAl₂O₄ is non-toxic, inexpensive, relatively high surface areas and these properties make them suitable for use as economically and environmentally viable solid heterogeneous catalysts. Generally, two main factors affecting the catalytic property of catalysts are the specific surface area and particle size, and typically a high surface area goes along with small particle size, which enhances the catalytic activity. The as-prepared samples were characterized by powder XRD, FT-IR, HR-SEM, HR-TEM, EDX, and VSM techniques and the obtained results are discussed.

2. Experimental part

2.1. Materials and methods

All the chemicals used in this study were of analytical grade obtained from Merck, India and were used as received without further purification. All chemicals such as nitrates of cobalt,

zinc and aluminium, and urea as the reducing agent were used for this method. In the preparation of $CoAl_2O_4$ samples, aluminium nitrate (10 mmol) and cobalt nitrate (5 mmol) were first dissolved in the urea solution under vigorous stirring at room temperature for 1 h until a clear transparent solution was obtained. Metal nitrate salts and the urea solution were chosen by considering the total reducing and oxidizing agent valences of the raw materials and were quantified in equivalence of NOx reduction (N_2O to N_2 , CO_2 and H_2O) at a low temperature. The precursor mixture of metal nitrates in urea solution was placed in a domestic microwave oven and exposed to the microwave energy in a 2.45 GHz multimode cavity at 850 W for 10 minutes. Initially, the precursor mixture boiled and underwent evaporation followed by the decomposition with the evolution of gases. When the solution reached the point of spontaneous combustion, it vaporized and instantly became a solid. After completion of the reaction, the obtained solid powder was then washed with ethanol and dried at 70 °C for 1h. The samples were prepared with the addition of Zn^{2+} of different molar ratios ($Zn-CoAl_2O_4$: x=0.0 and 0.5) to $CoAl_2O_4$. The obtained powders were used for further characterizations.

2.2. Characterization techniques

The structural characterization of spinel Zn-CoAl₂O₄ samples were performed using a Rigaku Ultima X-ray diffractometer (XRD) for 2θ values ranging from 10 to 80° using Cu-Kα radiation ($\lambda = 1.5418$ Å). The surface functional groups were analyzed by Perkin Elmer FT-IR spectrometer. The surface morphology of the samples was achieved at desired magnification with a Joel JSM 6360 high resolution scanning electron microscope (HR-SEM) equipped with energy dispersive X-ray (EDX) for elemental composition analysis. The transmission electron micrographs were carried out by Philips-TEM (CM20). Magnetic measurements were carried out at room temperature using a PMC MicroMag 3900 model vibrating sample magnetometer (VSM) equipped with 1 Tesla magnet.

3. Results and discussion

3.1. Powder XRD analysis

The crystal structure and phase purity of the powders were confirmed by analyzing the powder XRD patterns. Fig. 1 shows the XRD patterns of spinel Zn-CoAl₂O₄ nanoparticles. The characteristic peaks are corresponding to (220), (311), (222), (400), (331), (440), (620) and (533) diffraction planes. According to the XRD patterns, all diffraction peaks can be perfectly indexed

as face centered cubic spinel CoAl₂O₄ (JCPDS card no. 38-0812) [31]. The average crystallite size calculated from the most intense X-ray diffraction peak (311) using scherrer's Eq. (1),

$$D = \frac{0.89\lambda}{\beta\cos\theta} \qquad ---- (1)$$

where 'D' is the average crystallite size, ' λ ', the X-ray wavelength, ' θ ', the Bragg diffraction angle and ' β ', the full width at half maximum (FWHM). It was found that the average crystallite size was higher (20.65 nm) for pure CoAl₂O₄ while the crystallite size decreased from 15.72 nm to 14.13 nm for Zn-CoAl₂O₄ (x = 0 to 0.5). It can be seen that the widths of XRD peaks for the samples obtained at higher concentration of Zn-dopant (Zn_{0.5}Co_{0.5}Al₂O₄) are broader, indicating that the crystallite size is very smaller than other samples. The result reveals at Zn doping on CoAl₂O₄ sample controls and retards the growth of the crystallite size.

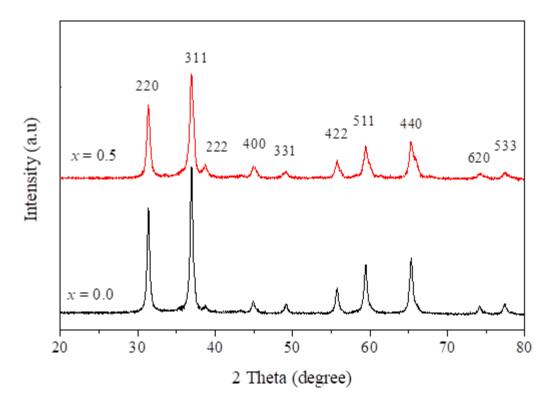


Fig. 1. Powder XRD patterns of Zn-CoAl₂O₄ nanoparticles

3.2 Fourier transform infrared (FT-IR) analysis

Fig. 2 shows the FT-IR spectra of spinel Zn-CoAl₂O₄ nanoparticles. A broad absorption band centered in the region 3100-3500 cm⁻¹, which can be assigned to the vibrations of water

 H_2O molecules. The absorption band at 2355 cm⁻¹ is due to the stretching vibration of CO_2 . A band at around 1630 cm⁻¹ is present in all compositions, which can be assigned to the H-O-H bending vibration. The bands at 825 cm⁻¹, 665 cm⁻¹ and 562 cm⁻¹ confirm the spinel structure of $CoAl_2O_4$. In all compositions of $CoAl_2O_4$ samples, the metal-oxygen stretching frequencies are reported in the range 500-900 cm⁻¹, associated with the vibrations of M-O, Al-O and M-O-Al bonds (M = Zn, Co) [26-33]. The results are in good agreement with the results obtained from the XRD analysis.

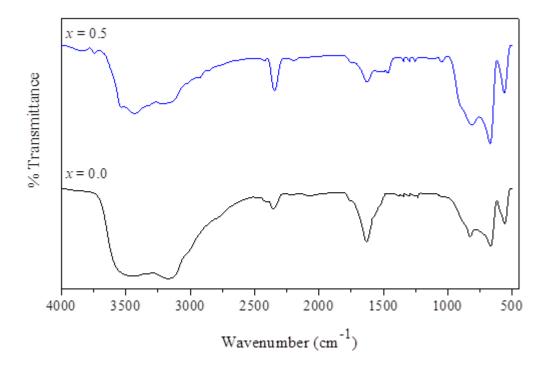


Fig. 2. FT-IR spectra of Zn-CoAl₂O₄ nanoparticles

3.3 Scanning electron microscopy (SEM) studies

The morphologies of spinel Zn-CoAl₂O₄ samples were confirmed by high resolution scanning electron microscope (HR-SEM) analysis. Fig. 3 shows HR-SEM images of Zn-CoAl₂O₄. HR-SEM images consist of agglomerated particle-like nano-crystals with uniform grain size smaller than 20 nm. It is believed that, during the combustion reaction, the microwave energy is used to nucleation growth of metallic Co²⁺ and Al³⁺ cations mixture obtained with a very short time was subjected in the microwave irradiation treatment to formed final products within few minutes of time with narrow size range was obtained [34].

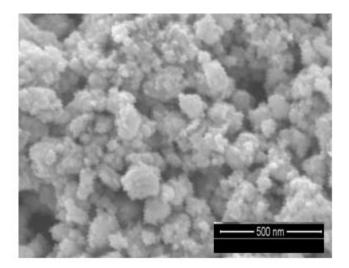


Fig. 3. SEM analysis of Zn-CoAl₂O₄ nanoparticles

3.4 Transmission electron microscopy (TEM) studies

The crystal structure, morphology and particle size of the samples were confirmed by high resolution transmission electron microscope (HR-TEM) analysis. Fig. 4 show the HR-TEM images of Zn_{.5}Co_{0.5}Al₂O₄ sample. It was confirmed that the samples consists of particle-like nano-crystals with small amount of agglomerations. However, these nanoparticles are in the range of 15-20 nm in diameter; these values are in good agreement with the values obtained from XRD data. The selected area electron diffraction (SAED) pattern of the sample Zn_{.5}Co_{0.5}Al₂O₄, presented in the Fig. 4, correspond to that of a spinel phase confirmation. The SAED pattern implies that the as-prepared spinel CoAl₂O₄ nano-crystals are good crystalline materials and single crystalline in nature.

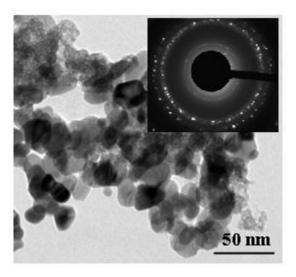


Fig. 4. TEM analysis of Zn-CoAl₂O₄ nanoparticles

3.5 EDX studies

Elemental composition of the samples was confirmed by Energy dispersive X-ray (EDX) analysis. Fig. 5 shows the EDX spectra of Zn-CoAl₂O₄. EDX results showed that the peaks of Co, Al and O elements in spinel CoAl₂O₄ samples, and there is no other peak, which confirmed the as-prepared samples are pure products. However, a small peak is appeared at 2.1 KeV for both samples, which indicated the presence of gold (Au) peak and it is has been used as a sputter (gold) coating, while preparing the sample for HR-SEM recording for the better visibility of the surface morphology.

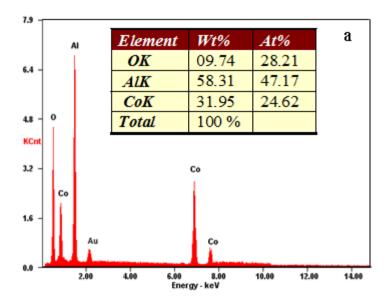


Fig. 5. EDX analysis of Zn-CoAl₂O₄ nanoparticles

3.6 VSM measurements

The magnetic behavior of spinel Zn-CoAl₂O₄ nanoparticles were investigated by using the external magnetic field between ± 15 kOe using room temperature vibrating sample magnetometer (VSM). Magnetizations (M) versus magnetic field (H) behavior plots are shown in Fig. 6. These M-H curves are typical for a soft magnetic material and indicate superpara (pure CoAl₂O₄) and weak ferromagnetism (Mn²⁺-doped CoAl₂O₄: x = 0.3 and 0.5), respectively, in the field ranges of ± 15 kOe. Pure and Mn²⁺-doped CoAl₂O₄ nanoparticles display 'hysteresis' type

curve and the magnetization decreased with increasing Zn^{2+} ions. However, it is observed that lower H_c and M_r values confirm that pure and Zn^{2+} in $CoAl_2O_4$ nanoparticles have soft nature of superpara and weak ferromagnetism respectively, due to the exchange between the ions occupying the tetrahedral and octahedral sites [33-36].

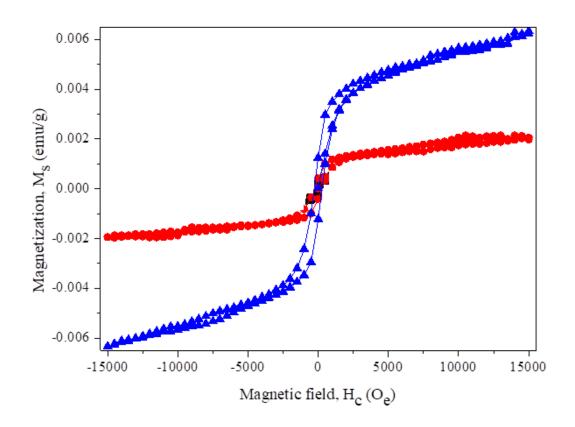


Fig. 6. VSM analysis of Zn-CoAl₂O₄ nanoparticles

4. Conclusions

Spinel Zn-CoAl₂O₄ NPs were successfully prepared by a simple MCM route using urea as the fuel. Effects of Zn²⁺ doping on structural, morphological, magnetic and catalytic properties were investigated. XRD, EDX and SAED results indicate that the as-synthesized samples have spinel structure without any other phase impurities. The appearance of broad band between 500 and 900 cm⁻¹ in FT-IR spectra revealed the formation of M-O, Al-O and M-O-Al bonds in the spinel structure. HR-SEM and HR-TEM images depicted the formation of well developed particle-like morphology with nano-sized grains below 20 nm. VSM studies revealed that the

Zn²⁺ in CoAl₂O₄ showed superpara-magnetism. Moreover, this method of preparation is economically and environmentally friendly approach.

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