e-ISSN 2320 –7876 www.ijfans.org
Vol.11, Iss.9, Dec 2022
Research Paper

One-pot microwave combustion synthesis, structural and magnetic characterization studies of spinel $CoAl_2O_4$ nanoparticles

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Abstract

Spinel $CoAl_2O_4$ nanoparticles were synthesized via *Opuntia dillenii* plant extract microwave heating method. *Opuntia dillenii* plant extract-assisted combustion method makes straightforward synthesis, which is alternative process of spinel nanoparticles preparation. The synthesized spinel $CoAl_2O_4$ nanoparticles was successfully characterized by powder XRD pattern, FT-IR spectra, EDX analysis, HR-SEM analysis, and VSM techniques. XRD pattern, FT-IR and EDX results established the development of spinel and single cubic phase $CoAl_2O_4$ nanocrystals. The formation of spherical shaped nanoparticles was confirmed by HR-SEM technique. VSM measurements revealed that $CoAl_2O_4$ sample have superparamagnetic behavior.

Keywords: Spinel $CoAl_2O_4$; Nanoparticles; *Opuntia dillenii* extract; Magnetic properties;

1. Introduction

Recently, nanostructured spinel type materials are attractive in materials science and nanotechnology, for the reason that of their novel physical, chemical and catalytic activities than that of their same bulkiness materials [1-5]. Among the various spinel materials, cobalt aluminate ($CoAl_2O_4$), has gained much attention in interdisciplinary areas due to their high mechanical strength, and chemical stability [6-8]. Various synthesis routes have been used to prepare the spinel type nanomaterials [8-10]. But the methods have some disadvantageous such as costly equipments and materials and difficult synthetic procedures. Recently, a facile microwave combustion method (MCM) has been used. In this route, the nanomaterials are synthesized at lower temperatures and also enough low cost with good controlled size of the products [10-12].

The present work focused on the synthesis of spinel $CoAl_2O_4$ nanoparticles by using green method on extract from *Opuntia dillenii* microwave combustion method [13-20]. To our knowledge, no literature is available on the synthesis of $CoAl_2O_4$ nanostructures by *Opuntia dillenii* plant extract microwave heating method. Nevertheless, *Opuntia dillenii* plant extracts using as the reducing agent by microwave heating method. Moreover, spinel $CoAl_2O_4$ nanomaterials are non-toxic, inexpensive, comparatively higher surface area and the properties formulate them proper for use as inexpensively and environmentally feasible solid heterogeneous nano-catalysts. The prepared sample was characterized by XRD, FT-IR, HR-SEM, EDX and VSM techniques and the achieved results are discussed.

2. Experimental

2.1. Materials and methods

Nitrates of cobalt and aluminum, and *Opuntia dillenii* plant extract as the raw materials were used by this method. Millipore water was used for this synthesis. *Opuntia dillenii*-extract was prepared from a 5 g piece of systematically washed *Opuntia dillenii* leaves were thinly cut and the gel obtained was liquefied in 10 ml of distilled water and stirred for 30 min to obtain solution, which is known as *Opuntia dillenii* plant extract. Nitrates of cobalt, and aluminum were dissolved in the *Opuntia dillenii* plant extract under stirring for 1 h and then located in a domestic microwave oven for 10 min. After completion of the reaction, the solid powder was then washed with wated ethanol and dried at 70 ºC for 1h. The obtained powders were labeled as $CoAl_2O_4$.

2.2. Characterization

The structural characterization of spinel $CoAl_2O_4$ nano-crystals were carry out using a Rigaku Ultima XRD (λ = 1.5418 Å). The functional groups were analyzed by Perkin Elmer FT-IR spectra. The morphology of the samples was achieved at desired magnification with a Joel JSM 6360 HR-SEM analysis. Magnetic properties were carried out using a PMC MicroMag 3900 model VSM.

2.3. Catalytic oxidation reaction

The oxidation of benzyl alcohol using nanocatalysts ($CoAl_2O_4$) was carried out in a batch reactor operated under atmospheric conditions. To a clean dry round bottom flask (10 mL) equipped with a reflux condenser and thermometer, and the flask containing 5 mmol of oxidant (H_2O_2). This was followed by the addition 0.5 g of $CoAl_2O_4$ nano-crystals and 5 mmol solvent. The mixture was stirred at 80 °C for 5 h. The progress of the reaction was monitored by GC. After completion of the catalytic oxidation reaction, the reaction mixture was cooled to room temperature and the catalyst was separated by filtration method. The products were identified by GC-MS.

3. Results and discussion

3.1. Powder XRD analysis

The crystal structure, crystallite size and phase formation of the powders were established by analyze the powder XRD pattern. Fig. 1 shows the XRD pattern of spinel $CoAl_2O_4$ nanoparticle. The peaks of 31.13, 36.84, 38.64, 44.53, 49.14, 55.73, 59.43, 65.53, 74.25 and 77.52° can be absolutely indexed as fcc spinel $CoAl_2O_4$ (JCPDS card no. 38-0814).

The crystallite size was calculated using Scherrer's Eq. (1),

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

where 'D' the crystallite size, 'λ' is the X-ray wavelength, 'β' is the full width at half maximum (FWHM) and 'θ' is the Bragg diffraction angle. The calculated average crystallite size of the sample is 18.35 nm.

e-ISSN 2320 –7876 www.ijfans.org
Vol.11, Iss.9, Dec 2022

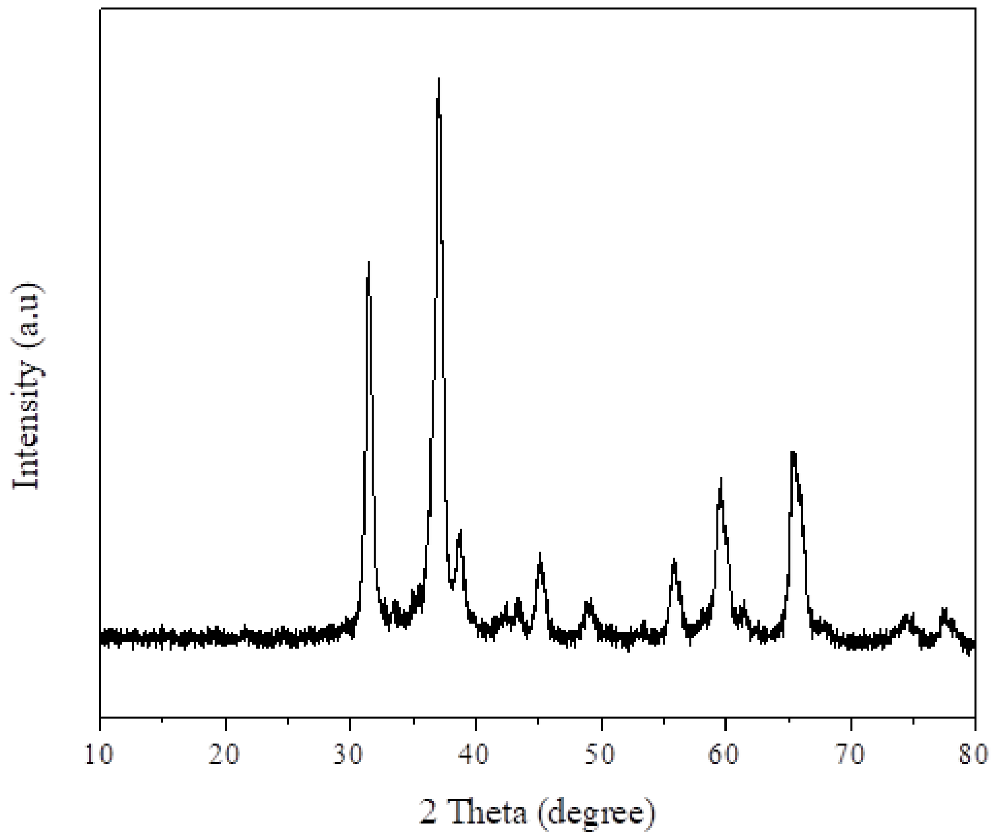


Figure 1. Powder XRD pattern of spinel $CoAl_2O_4$ sample.

3.2 FT-IR analysis

Fig. 2 shows the FT-IR spectra of spinel $CoAl_2O_4$ nanoparticle. A wide-ranging band appeared in the expanse 3220-3440 cm^{-1} showed the vibrations of water H_2O molecules. A band at around 1630 cm^{-1} assigned H-O-H vibration. The absorption band at 2357 cm^{-1} is due to the CO_2 molecule stretching vibration. The M-O stretching bands are observed in the range 550-850 cm^{-1}, connected to the Al-O and Co-O-Al bonds [14-20].

e-ISSN 2320 –7876 www.ijfans.org
Vol.11, Iss.9, Dec 2022

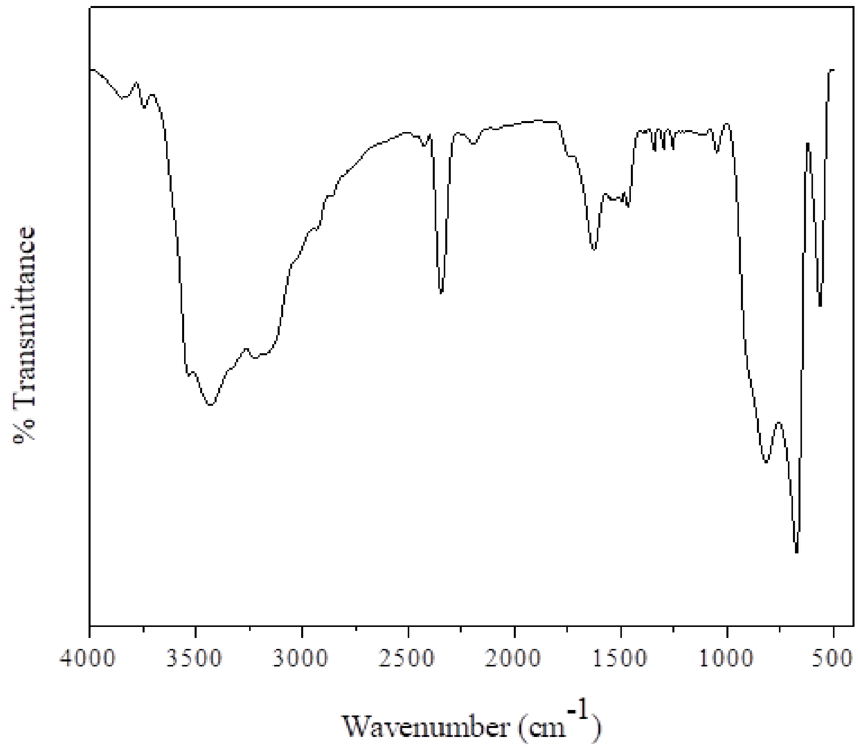
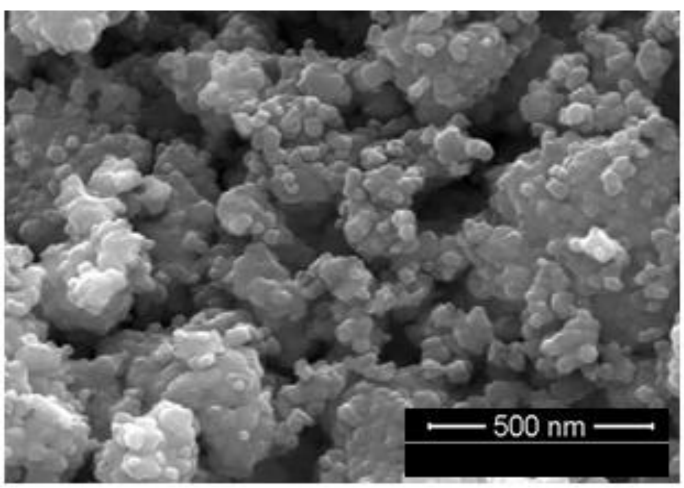


Figure 2. FT-IR spectra of spinel $CoAl_2O_4$ sample.

3.3 SEM studies

The morphology of spinel $CoAl_2O_4$ sample was confirmed by HR-SEM analysis. Fig. 3 shows HR-SEM image of $CoAl_2O_4$ sample. HR-SEM image clearly shows the agglomerated particle-like nano-crystals with irregular grain size smaller than 50 nm. From the results, it is assumed that, during the microwave heating process, the microwaves are involved for nucleation and formed the final products with narrow size range of particles within few minutes.



e-ISSN 2320 –7876 www.ijfans.org
Vol.11, Iss.9, Dec 2022

Figure 3. HR-SEM image of spinel $CoAl_2O_4$ sample.

3.4 EDX studies

Elemental and phase purity was confirmed by EDX spectral analysis. Fig. 4 shows the EDX spectra of $CoAl_2O_4$. EDX results showed that the peaks of Co, Al and O elements and there is no other secondary peak, which established the pure product formation.

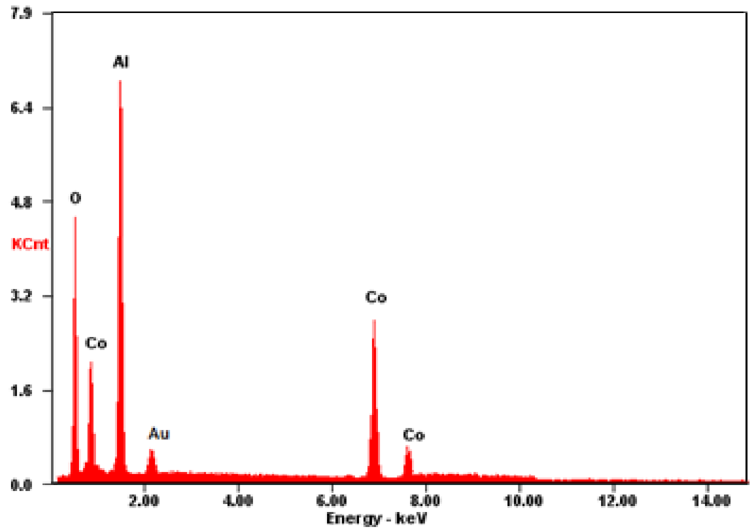


Figure 4. EDX spectra of spinel $CoAl_2O_4$ sample.

3.5 VSM measurements

The magnetic activities of spinel $CoAl_2O_4$ nanoparticle was analyzed through external field between ±10 kOe by VSM at room temperature. Magnetization (M) versus applied field (H) curve is shown in Fig. 5. From the M-H curve, we can infer that a soft magnetic nature of $CoAl_2O_4$ material and also indicate superparamagnetism at ±15 kOe. The obtained results show that the value of M_s is 1.45×10^{-4} emu/g. However, it is noted that lower M_s, H_c and M_r values confirmed the $CoAl_2O_4$ nanoparticles have soft nature of superparamagnetism [21-27].

e-ISSN 2320 –7876 www.ijfans.org
Vol.11, Iss.9, Dec 2022

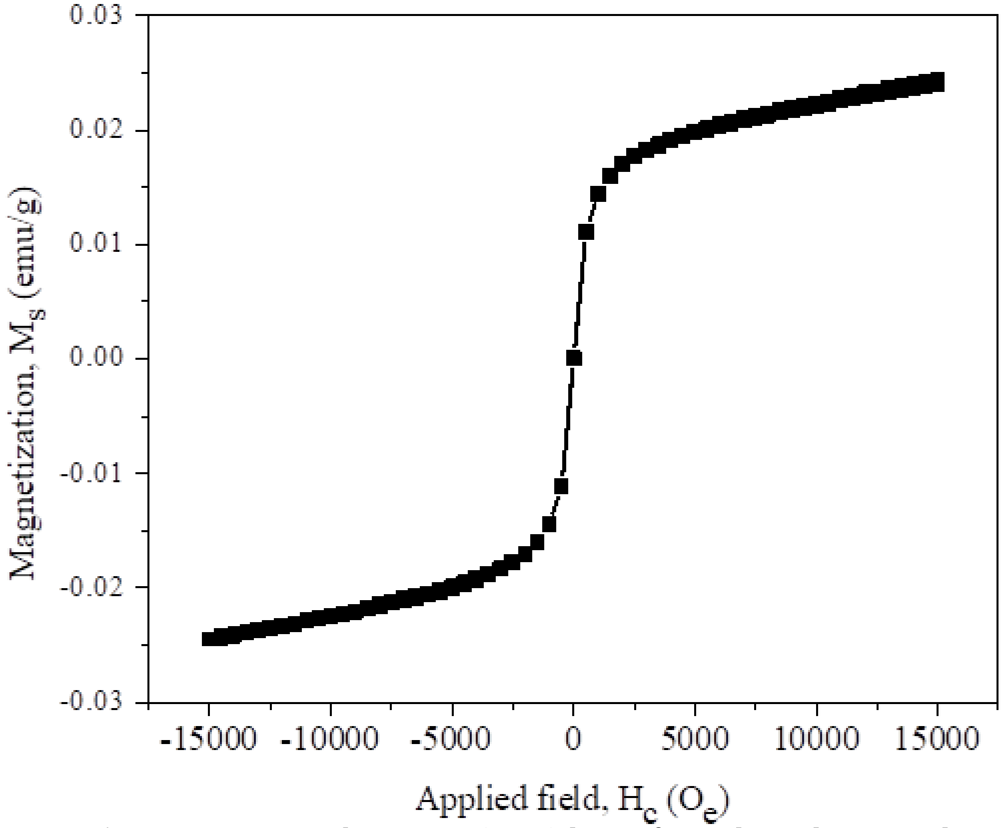


Figure 5. Magnetic hysteresis (M-H) loop of spinel $CoAl_2O_4$ sample.

3.6. Catalytic oxidation of alcohols

The catalytic performance of $CoAl_2O_4$ nanoparticle was evaluated in the oxidation of alcohols (benzyl alcohol) in presence of 30 % H_2O_2 as oxidant. Catalytic results showed that the particle size and surface area of the catalyst had a strong influence on both the conversion and product selectivity. In the catalytic oxidation reaction, alcohols (5 mmol), H_2O_2 (5 mmol) as the oxidant were added with 0.5 g of catalyst and the contents were heated at 80 °C in the presence of acetonitrile (5 mmol) as the solvent for 5 h. It was found that the conversion and product selectivity of alcohols into carbonyls for the sample $CoAl_2O_4$ nanoparticle was higher. It is mainly due to the uniform distribution with smaller particle size of nano-sized $CoAl_2O_4$ nanoparticle [28-30]. The oxidation of benzyl alcohol into benzaldehyde was achieved with 92.35 % conversion and 100 % selectivity of benzaldehyde using the $CoAl_2O_4$ nanoparticle catalyst.

e-ISSN 2320 –7876 www.ijfans.org
Vol.11, Iss.9, Dec 2022

3.7. Reusability studies

Nowadays, heterogeneous catalysis has been used in many industrial. However, catalyst reusability is of major importance for industrial applications. For this purpose, the catalyst recycling experiments were achieved by fixing the catalyst magnetically at the bottom of the flask, and the solution was decanted after each run. The left solid was washed several times with ethanol and dried at 120 °C in an air oven for half an hour and introduced into the flask allowing the system to proceed for next runs under the identical conditions [29-33]. The catalyst ($CoAl_2O_4$ nanoparticle) was repeatedly reused five times without any evident loss of its catalytic activity, indicating that the catalyst displays good reproducibility and stability.

4. Conclusions

Spinel $CoAl_2O_4$ nano-catalysts were prepared by a easy microwave heating route using *Opuntia dillenii* plant extract. Powder XRD and EDX results specified that the prepared sample has a spinel without any secondary phase impurities. The manifestation of wide-ranging band between 550 and 850 cm^{-1} in FT-IR spectra exposed the arrangement of Al-O and Co-O-Al bonds appeared in the spinel. HR-SEM image showed the construction of well residential particle morphology with nano-sized grains. VSM studies revealed that $CoAl_2O_4$ showed superparamagnetism. It was found that $CoAl_2O_4$ nanoparticle is highly active towards the selective oxidation of benzyl alcohol into benzaldehyde at a low temperature with very high yield, due to the higher surface area and number of active sites.

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