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Synthesis, characterization of nickel aluminate nanoparticles by microwave combustion method and their catalytic properties

C. Ragupathi [a], J. Judith Vijaya [a,*], L. John Kennedy [b]

[a] Catalysis and Nanomaterials Research Laboratory, Department of Chemistry, Loyola College (Autonomous), Chennai 600034, India
[b] Materials Division, School of Advanced Sciences, Vellore Institute of Technology (VIT) University, Chennai Campus, Chennai 600127, India

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ABSTRACT

Microwave combustion method (MCM) is a direct method to synthesize $NiAl_2O_4$ nanoparticles and for the first time we report the using of *Sesame* (*Sesame indicum* L.) plant extract in the present study. Solutions of metal nitrates and plant extract as a gelling agent are subsequently combusted using microwave. The structure and morphology of $NiAl_2O_4$ nanoparticles are investigated by X-ray diffraction (XRD), Fourier transforms infrared spectra (FT-IR), high resolution scanning electron microscopy (HR-SEM), energy dispersive X-ray analysis (EDX), high resolution transmission electron microscopy (HR-TEM), diffuse reflectance spectroscopy (DRS) and photoluminescence (PL) spectroscopy, Brunauer–Emmett–Teller (BET) analysis and vibrating sample magnetometer (VSM). XRD pattern confirmed the formation of cubic phase $NiAl_2O_4$. The formation of $NiAl_2O_4$ is also confirmed by FT-IR. The formation of $NiAl_2O_4$ nanoparticles is confirmed by HR-SEM and HR-TEM. Furthermore, the microwave combustion leads to the formation of fine particles with uniform morphology. The magnetic properties of the synthesized $NiAl_2O_4$ nano and microstructures were investigated by vibrating sample magnetometer (VSM) and their hysteresis loops were obtained at room temperature. Further, $NiAl_2O_4$ prepared by MCM using *Sesame* (*S. indicum* L.) plant extract is tested for the catalytic activity toward the oxidation of benzyl alcohol.

1. Introduction

Metal oxides have attracted considerable attention in the past decade, because of their unique chemical and physical properties leading to a numerous potential applications, such as, nanoscale electronic and optoelectronic devices [1]. The oxidation of alcohols into carbonyl compounds (aldehydes and ketones) is a significant transformation in organic chemistry with recognized industrial importance. Aldehydes and ketones are important raw materials and intermediates for the synthesis of many fine chemicals, such as, dyes, medicines, and perfumes, etc. One of the most important routes to aldehydes and ketones is the selective oxidation of their corresponding alcohols and a suitable catalyst always plays an important role in these reactions [2,3].

The general formula of spinels is AB_2O_4. In the spinel structure, the anions are arranged in a cubic close packed array with the cations arranged in the sites of the array. There are eight tetrahedral and four octahedral sites per molecule. $NiAl_2O_4$ is a mixed oxide with normal spinel structure, where Al occupies the octahedral sites, and Ni occupies the tetrahedral sites in the spinel structure [4]. In case of inverse spinels, one half of A^{2+} ions occupy the tetrahedral holes and the remaining A^{2+} ions and all B^{3+} ions occupy the octahedral sites. Investigation of the cation distribution in spinels, among the tetrahedral and octahedral sites is an important subject, because some properties such as magnetic, semiconducting, catalytic, etc. of spinels are determined by the cation sites.

$NiAl_2O_4$ can be prepared by different methods such as solid-state reaction [5], impregnation, co-precipitation [6] and sol–gel method [7]. The combustion method is very facile and only takes a few minutes, and it has been widely applied to the preparation of various nano-scale oxide materials. This synthetic technique makes use of the heat energy liberated by the redox exothermic reaction at a relative low igniting temperature between the metal nitrates and urea or other fuels such as, the plant extract. Furthermore, the combustion method is also safe, instantaneous and energy saving.

The advantage of microwave combustion method is that it leads to a highly exothermic reaction, which in turns led to a direct formation of spherical particles. The microwave heating causes the uniform distribution of temperature between the surface and the bulk material, and there by leading to the fast formation of nanoparticles. The microwave dielectric heating has resulted in acceleration of the chemical transformations in a microwave field, which cannot be achieved easily by the conventional method. Moreover, high

* Corresponding author. Tel.: +91 44 28178333; fax: +91 44 28175566.
E-mail addresses: jjvijayaloyola@yahoo.co.in, jjvijaya78@gmail.com (J.J. Vijaya).

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reaction temperature is achieved under microwave irradiation that causes the increase in the chemical reaction rate along with the controlled spherical shapes. On the other hand, the collision efficiency is effectively influenced by the mutual orientation of polar molecules involved in the reaction, which further depends upon the vibration frequency of the atoms at the reaction interface. Thus, it can be postulated that the microwave field has an overall influence on the reaction rate and nanoparticle size along with the shape control [8].

Recently, the plant extract has been used as both reducing and gelling agent for the synthesis of metal oxides. The plant extract plays a fuel role, but also has a coordinating action, capturing the involved metal ions in the amylose helix of the plant extract and impeding the separation of metal oxides. Nanoparticle synthesis using the microorganisms, enzymes, and plant extracts have been suggested as the possible ecofriendly alternatives to phytosynthesis. The choice of an environmentally compatible solvent system, an eco-friendly reducing agent, and a nonhazardous gelling agent for stabilizing the nanoparticles are three main criteria required for a nanoparticle synthesis [9,10].

Sesame (*Sesame indicum* L.,) pedaliaceae has been used extensively as a traditional food in the orient for various purposes and commonly known as sesame. *Sesame* (*Sesamum indicum* L.,) is an important oilseed crop that is cultivated for its edible oil, protein, vitamins, antioxidants and amino acids. Natural antioxidants, such as, flavonoids, tannins, coumarins, curcumanoids, xanthons, phenolics, lignans and terpenoids are found in the various plant products (fruits, leaves, seeds and oils), and they are known to protect easily oxidizable constituents from oxidation. Hence, there is a tendency toward the use of natural antioxidants of plant origin to replace these synthetic antioxidants. *S. indicum* L., may be used as a reducing agent in the preparation of metal oxide precursor powders. The advantage of this method includes the use of inexpensive, nontoxic and environmentally sympathetic precursors, simple and time saving procedure [11–13].

Present method of sample preparation ensures a high chemical homogeneity, due to the solution mixture of initial reagents and, as a result, it favors the production of desired phases. Among the soft-chemistry techniques, combustion method requires relatively shorter reaction times and lower temperatures. Moreover, the combustion synthesis methods have been advantageous over the other solid-state synthesis in terms of better compositional homogeneity and purity of the final product. Accordingly, a series of combustion decomposition techniques are developed to yield single-phase, multicomponent ceramics as well as complex compound oxide phases in homogeneous form at relatively low temperatures [14,15].

Investigations on different scale nano-microstructures and respective morphologies of $NiAl_2O_4$ nanoparticles are still warranted. Hence, in the present study, we have employed a simple and rapid microwave assisted combustion method to synthesize $NiAl_2O_4$ nanoparticles using *S. indicum* L., plant extract as a fuel. The whole process takes only a few min to yield the $NiAl_2O_4$ nanoparticles. The structure, morphology, optical and magnetic properties of the as-prepared $NiAl_2O_4$ nanoparticles were investigated by XRD, FT-IR, HR-SEM, EDX, TEM, DRS, PL and VSM spectra, respectively. Later, $NiAl_2O_4$ samples prepared by MCM are tested for their catalyst activity toward the oxidation of benzyl alcohol.

2. Experimental

2.1. Materials

Nickel nitrate and aluminum nitrate were used as the starting material, (Merck chemicals, India) and were used without the further purification. The *Sesame* (*S. indicum* L.) leaves were collected from the local agricultural fields in Chennai, Tamilnadu.

2.2. Plant extracts preparation Sesame (Sesamum indicum L.,)

A 5 g portion of thoroughly washed *Sesame* (*S. indicum* L.) leaves were finely cut and the obtained gel was dissolved in 17 ml of deionized water, and stirred for 40 min to obtain a clear solution. The resulting extract was used as a *Sesame* (*S. indicum* L.) plant extract solution.

2.3. Synthesis of nickel aluminate by MCM

In the first step, stoichiometric amounts of highly purified metal nitrates 7.502 g of aluminum nitrate and 2.974 g nickel nitrate (Al:Ni = 2:1) were dissolved in distilled water [16], and then mixed with *Sesame* (*S. indicum* L.) plant extract solution under the constant stirring for 5 h, at room temperature, until a clear transparent solution was obtained. The molar ratio of Ni/Al was kept as 1:2. The clear transparent solution was placed in a domestic microwave-oven (2.45 GHz, 950 W) for 18 min. Initially, the solution boiled and underwent dehydration followed by the decomposition with the evolution of gases. After the solution reaches the point of spontaneous combustion, it vaporizes the solution instantly and becomes a solid. The obtained solid was washed well with alcohol and dried. During the course of the microwave assisted combustion synthesis using a microwave oven operated at a power of 950 W a temperature from 400 to 600 °C [17], is developed, which would have resulted in the spontaneous combustion to form the products.

Metal nitrate salts and the plant extract (used in the mixture) were chosen by considering the total reducing and oxidizing agent valences of the raw materials, and were quantified in equivalence of NO_x reduction (N_2O to N_2) at low temperatures and phase pure, and fully crystallized $NiAl_2O_4$ was obtained for both the compositions, during the microwave method itself without the need of further calcinations at higher temperature. However, microwave heating involves the absorption and/or linear coupling of the microwave field followed by the 'conversion' of electromagnetic energy into the thermal energy. In this technique, there is no thermal conduction process involved. This is due to the fact that the heat is generated internally within the sample.

2.4. Characterization of nickel aluminate

The structural studies were carried out using a Philips X' pert diffractometer for 2θ values ranging from 10 to 80° using Cu Kα radiation at λ = 0.154 nm. A Perkin Elmer infrared spectro photometer was used for the determination of the surface functional groups. The morphological studies and energy dispersive X-ray analysis of nanomaterials have been performed using a Joel JSM6360 high resolution scanning electron microscope. Stereo-scan LEO 440 and a high resolution transmission electron microscope. The nitrogen adsorption–desorption isotherms of the sample was measured using an automatic adsorption instrument (Quantachrome Quadrawin gas sorption analyzer) for the determination of surface area and total pore volumes. The diffuse reflectance UV–visible spectra of the nanomaterials was recorded using Cary 100 UV–visible spectrophotometer. The emission properties were recorded using Varian Cary Eclipse Fluorescence spectrophotometer.

2.5. Catalytic test

The oxidation of benzyl alcohol was carried out in a batch reactor operated under atmospheric conditions. 10 mmol of oxidant (H_2O_2) was added along with a 0.5 g of the nano nickel aluminate and the