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Nanostructured copper aluminate spinels: Synthesis, structural, optical, magnetic, and catalytic properties

C. Ragupathi [a], J. Judith Vijaya [a,*], L. John Kennedy [b], M. Bououdina [c,d]

[a] Catalysis and Nanomaterials Research Laboratory, Department of Chemistry, Loyola College, Chennai 34, India
[b] Materials Division, School of Advanced Sciences, Vellore Institute of Technology (VIT) University, Chennai Campus, Chennai 127, India
[c] Nanotechnology Centre, University of Bahrain, PO Box 32038, Bahrain
[d] Department of Physics, College of Science, University of Bahrain, PO Box 32038, Bahrain

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ABSTRACT

Copper aluminate nanostructured materials were synthesized by a microwave combustion method (MWCM) using the plant extract (*aloe vera*) as a fuel without using any other template or surfactant. For comparison, it was also prepared by using the conventional combustion method (CCM). The as-synthesized copper aluminate was characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), high resolution scanning electron microscopy (HR-SEM), energy dispersive X-ray analysis (EDX), diffuse reflectance spectroscopy (DRS), photoluminescence (PL) spectroscopy, nitrogen adsorption/desorption isotherms, and vibrating sample magnetometer (VSM). The results indicated that the copper aluminate nanomaterials obtained by MWCM shows good crystallinity with the uniform size distribution than the ones prepared by CCM. The XRD and FT-IR results confirmed the crystal structure of copper aluminate. The formation of copper aluminate nano- and microstructures were confirmed by HR-SEM. The optical absorption and photoluminescence emissions were determined by DRS and PL spectra, respectively. The effect of the catalyst and the oxidant on the catalytic oxidation of benzyl alcohol was also investigated.

1. Introduction

Among the various inorganic solids, spinel-type mixed oxides (AB_2O_4) are well known for their excellent catalytic action. These oxides are non-toxic, inexpensive and very stable materials with strong resistance to acids and alkalis. They possess high melting point and relatively high surface area in the range 10–100 m^2/g. Mixed metal oxides have long been a topic of interest, because of their application as magnetic materials, pigments, catalysts and refractory materials. Aluminate spinels have high thermal stability, high mechanical resistance, hydrophobicity and low surface acidity [1,2]. Several studies have suggested that metal oxide nanostructures may function as active species in various organic reactions. Recent reports [3] have revealed that the supported metal nanostructures have attractive catalytic performances for the oxidation of alcohols. Liquid phase oxidation of benzyl alcohol is a hot topic in modern organic synthesis. The design and development of a catalyst with high conversion and selectivity for the catalytic oxidation must also be carried out with regard to the preservation of oil related resources.

For selective oxidation reactions, there is a tremendous challenge to prevent over oxidation of the products, which

* 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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are often more sensitive to be oxidized than the reactants. The direct oxidation of benzyl alcohol to benzaldehyde is such type of reaction. Benzaldehyde is a chief raw material for many useful chemicals, such as dye, resin, fragrance and drugs, in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives. It is also an important intermediate for the processing of perfume and flavoring compounds and for the preparation of certain aniline dyes. Liquid phase hydrogen peroxide is a highly attractive oxidant because it is a cheap, mild and environmentally benign reagent with a high content of 'active' oxygen, and water is the only by-product.

In general, combustion based method is an easy and convenient method for the preparation of a variety of advanced ceramics, catalysts and nanomaterials. Through the combustion-based method, it is possible to produce the monophasic nanopowders with homogeneous structure at lower temperatures with shorter reaction times [4]. Moreover, solution based methods have been reported for the preparation of copper aluminate nanoparticles that include polymeric precursor method [5], combustion [6] and sol–gel method [7].

Microwave-processing of materials is fundamentally different from the conventional processing, due to its different mechanism. In a microwave oven, due to the interaction of microwaves with the material, heat is generated within the sample. However, in conventional heating, the heat is generated by an outside source, and then it is transferred to the surface sample. The microwave method has been proved and accepted as a promising method for the volumetric heating, high-reaction rate and selectivity, short-reaction time, and high yield when compared to the conventional method. This opened up the possibility of the preparing materials in a very short time with high-energy efficiency [8]. Compared to the other techniques, the microwave method is a useful and attractive technique for the preparation of copper aluminate, because of the fact that pure and ultrafine powders can be produced at relatively low temperatures.

Recently, plant extract has been used as both reducing and capping agent for the synthesis of nanomaterials. There are many reports on the synthesis of metal and semiconductor nanoparticles using fungi, actinomycetes and plant extracts [9]. *Aloe vera* plant extract has been successfully used to synthesize single nanocrystalline triangular gold and silver nanoparticles in high yield by the reaction with aqueous metal ions source (chloroaurate ions for Au and silver ions for Ag). The plant extract not only plays a fuel role, but also as a coordinating agent, capturing the involved metal ions in the amylose helix of the extract in well-defined sites, and impeding the separation of metal oxides. An appealing topic of this research field is the non-polluting and controlled synthesis of oxide materials, which involves a low cost natural compound as a raw material and also as an active ingredient in the preparation of nanosized metal oxide particles [10,11].

Aloe vera (*Aloe barbadensis Miller*) is a perennial succulent belonging to the Liliaceal family, and is a cactus-like plant that grows in hot and dry climates. *Aloe vera* gel is colorless, and present in the inner part of the fresh leaves. The chemical composition of aloe vera plant is largely dependent on the species analyzed. A prominent feature of an *Aloe vera* is its high water content, ranging from 97.5% to 99.5% of fresh matter [12]. *Aloe vera* plant extract contains water, fat-soluble vitamins, minerals, enzymes, polysaccharides, phenolic compounds and organic acids. More than 60% of the remaining solid is made up of polysaccharides [13]. *Aloe vera* plant extract may be used as a bio-reducing agent in the preparation of metal oxide precursor powders. Most recently, Maensiri et al. [14] reported for the first time, the synthesis of In_2O_3 nanoparticles using *aloe vera* plant extract. This is due to the presence of long chain polysaccharides in the *aloe vera* plant extract that affords the homogeneous distribution of metal oxides. Most recently, there is another report on $ZnAl_2O_4$ formation by using the plant extract with tunable sizes/morphologies [15].

Hence, in the present study, we prepared copper aluminate by two different methods viz. CCM and MWCM using aloe vera plant extract for the comparative investigation of their structural, optical, magnetic and catalytic properties. The prepared copper aluminate nanostructures were characterized by X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FT-IR), high resolution scanning electron microscopy (HR-SEM), energy dispersive X-ray analysis (EDX), and high resolution transmission electron microscopy (HR-TEM), nitrogen adsorption/desorption isotherms. The magnetic behavior of the samples was studied by a vibrating sample magnetometer (VSM), and the optical studies were carried out by diffuse reflectance spectroscopy (DRS), and photoluminescence studies (PL). Finally, the samples were tested for their catalytic activity towards the oxidation of benzyl alcohol.

2. Experimental section

2.1. Synthesis of copper aluminate by conventional and microwave combustion method

Copper nitrate and aluminum nitrate were used as the starting materials (Merck chemicals, India) without further purification. The aloe vera leaves were collected from the local agricultural fields, Ariyalur, Chennai and Tamilnadu. 3 g of thoroughly washed aloe vera leaves were cut finely and the gel obtained was dissolved in 10 ml of de-ionized water and stirred for 40 min to obtain a clear solution. The resulting product was used as *aloe vera* plant extract (AVPE).

Copper and aluminum nitrates were dissolved in de-ionized water, and then mixed with the AVPE under the constant stirring for 5 h at room temperature until a clear transparent solution was obtained. The molar ratio of Cu/Al was kept as 1:2. An AVPE was mixed with the nitrate mixtures. AVPE solution has a double function of both reducing and gelling agent for the synthesis of mixed metal oxides. Metal nitrate salts and the AVPE 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, CO_2 and H_2O) at a low temperature. The solution was dried in an oven at 160 °C for 5 h. The powders thus obtained were then sintered at 500 °C at a heating rate of 5 °C/min for 3 h in