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Highly selective oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide by cobalt aluminate catalysis: A comparison of conventional and microwave methods

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Abstract

A comparative study of the structural, optical and catalytic properties of $CoAl_2O_4$ nanoparticles is reported. Cobalt aluminate ($CoAl_2O_4$) nano and microstructures were synthesized by both conventional and microwave methods using *Sesame* (*Sesamum indicum,* L.,) as a plant extract. The use of *Sesame* extract provides an alternative method for a simple and economical synthesis of cobalt aluminate. Synthesized cobalt aluminate powder were characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption/desorption isotherms, diffuse reflectance spectroscopy (DRS), and photoluminescence (PL) studies. $CoAl_2O_4$ prepared by the microwave method was found to possess a higher surface area, and lower crystallite size than the one prepared by the conventional method, which in turn leads to the improved performance towards the selective oxidation of benzyl alcohol to benzaldehyde.

Keywords: Cobalt aluminate; Nanoparticles; Surface area; Oxidation; Benzyl alcohol

1. Introduction

Spinel structured oxide materials have gained considerable attention in the material science field, because of their interesting properties, such as, magnetic, semiconducting, catalytic, and optical properties [1]. Attention was first drawn to their optical properties, since $CoAl_2O_4$ has been a historic blue pigment for a long time till today, for instance as a contrast-enhancing luminescent pigment. Cobalt aluminate powders have been widely used as inorganic ceramic blue pigments (Thenard's Blue) [2]. 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 holes of the array. There are eight tetrahedral and four octahedral holes per molecule. In case of normal spinels, the A^{2+} ions occupy the tetrahedral holes and B^{3+} ions are present in the octahedral holes. In case of inverse spinels, one half of A^{2+} ions occupy the tetrahedral holes and the remaining A^{2+} and all B^{3+} ions occupy the octahedral holes. Cobalt aluminates are also of great interest in the field of heterogeneous catalysis. $CoAl_2O_4$ has the normal spinel structure in which Co^{2+} ions are accommodated in tetrahedral positions, while Al^{3+} ions are in octahedral positions [3].

The major area of organic synthesis deals with the selective oxidation of alcohols to aldehydes. Among these, aromatic aldehydes are important for the preparation of fragrances and flavors, hence, a lot of attention is given to their effective production. Liquid phase oxidation of benzyl alcohol to benzaldehyde has widely attracted the researchers, because it has tremendous applications in cosmetics, perfumery, food, dye stuff, agrochemical and pharmaceutical industries. It is considered as the second most important aromatic molecule after vanillin [4]. Liquid phase oxidation of

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benzyl alcohol using hydrogen peroxide is more convenient, because the oxidant has high content of active oxygen and is cheap, mild and environmentally benign [5].

Recently, $CoAl_2O_4$ has been prepared by a number of methods, such as co-precipitation [6,7], sol–gel [8,9], hydrothermal synthesis [10,11], and low temperature combustion [12]. Microwave technique is extensively used for the synthesis of various nanomaterials. Since, microwave heating is an in situ mode of energy conversion; they are fundamentally different from the conventional heating processes. In a microwave oven, due to the interaction of micro-waves with the material, the heat is generated within the sample itself. In conventional method, the heat is generated by heating the elements, and then it is transferred to the sample surface [13]. The use of microwave method has several advantages. The foremost of which are the shortened periods of synthesis, enhanced reaction kinetics, and the reactant selectivity, during the energy transfer from the microwave field, which assists the stabilization of the metastable phase of the material [14].

Nowdays, the plant extract has been used as both reducing and gelling agent for the synthesis of metal oxides. The plant extract plays not only a fuel role, but also has a coordinating action, capturing the involved metal ions in the amylose helix of the plant extract, impeding the separation of metal oxides [15]. *Sesame indicum* L., has been used extensively as a traditional food in the orient for various purposes and commonly known as sesame. *Sesame* (*S. indicum*) 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, sucrose, tartaric, oxalic acid and terpenoids are found in various plant products (fruits, leaves, seeds and oils, and they are known to protect easily oxidizable constituents from oxidation. Hence, there is a tendency towards 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. [16].

In this work, cobalt aluminate nanoparticles were obtained by both microwave method and conventional method. Benzyl alcohol oxidation tests were carried out to study the influence of the preparation method on the catalytic activity of the nano $CoAl_2O_4$ samples. The best activity and selectivity towards the catalytic oxidation were observed from the one prepared by a microwave method.

2. Experimental section

2.1. Materials

Cobalt nitrate (98% purity) and aluminum nitrate (97% purity) were used as the starting material, (Merck chemicals, India) and were used as received without further purification. The *Sesamum* (*S. indicum* L.) leaves were collected from local agricultural fields, Ariyalur, Chennai, Tamilnadu.

2.2. Preparation of the plant extract

The fresh green leaves, *Sesamum* (*S. indicum* L.) were washed three times with ultra-pure water to remove the unwanted dust particles. The leaf extract used for the synthesis was prepared as follows: 50 g of thoroughly washed leaves is taken in 250 ml beaker, boiled, and stirred in 100 ml ultra-pure water for 45 min to obtain the clear solution. The resulting solution is called as *Sesamum* extract.

2.3. Synthesis of cobalt aluminate

Cobalt nitrate and aluminum nitrate were dissolved in deionized water and then mixed with *Sesamum* (*S. indicum* L.) extract under constant stirring for 5 h, at room temperature until a clear transparent solution was obtained. The molar ratio of Co/Al was kept as 1:2. The solution was dried in an air oven at 170 °C for 3 h. The powders were then sintered at 600 °C at a heating rate of 5 °C/min for 3 h in a muffle furnace and was labeled as sample A (prepared by CM).

The above-said clear transparent solution was placed in a domestic microwave-oven (2.45 GHz, 900W) for 20 min. Initially, the solution boiled and underwent dehydration followed by the decomposition with the evolution of gases. It vaporized the solution and instantly became a solid, and it was labeled as sample B (prepared by MM).

2.4. Characterization of nano cobalt aluminate

The structural studies were carried out using a Philips X'pert diffractometer for 2θ values ranging from10 to 80° using Cu $K\alpha$ radiation at $\lambda = 0.154$ nm. A Perkin Elmer infrared spectrophotometer was used for the determination of the surface functional groups of the nanomaterials. Morphological studies and energy dispersive X-ray analysis have been performed using a Jeol JSM6360 scanning electron microscope. The samples were coated with gold by a gold sputtering device for the better visibility of the surface morphology. Transmission electron microscopy, TEM, (CM200 FEG PHILIPS) was used to determine the shape and the average size of the crystallites. The N_2 adsorption–desorption isotherms of the samples were measured by the using an automatic adsorption instrument (Quantachrome Quadrawin gas sorption analyzer) for the determination of surface area and total pore volume. The diffuse reflectance UV–Visible spectra of the nanomaterials were recorded using Cary100 UV–Visible spectrophotometer. The emission properties were recorded using Varian Cary Eclipse Fluorescence spectrophotometer. The oxidized product after the catalytic reaction is collected and studied using Agilent GC technique. The column used for the study was DB wax column (capillary column) of length 30 mm and helium was used as the carrier gas.

2.5. Catalytic test

The oxidation of benzyl alcohol was carried out in a batch reactor operated under atmospheric conditions. 5 mmol of oxidant (H_2O_2) was added along with 0.5 g of the cobalt aluminate (sample A and sample B), and the contents were heated at 80 °C in acetonitrile medium for 5 h in a three necked round bottom flask equipped with a reflux condenser and thermometer.