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Synthesis and characterization of nanocrystalline zinc aluminate spinel powder by sol–gel method

Ravi Kant Sharma, Ranjana Ghose*

Department of Chemistry, Indian Institute of Technology (B.H.U), Varanasi 221005, India

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Abstract

Single-phase nanocrystalline zinc aluminate ($ZnAl_2O_4$) spinel powder has been synthesized by the sol–gel method. Zinc aluminate nanoparticles were formed at 600 °C, which is at much lower temperature than by solid state reactions. Formation of $ZnAl_2O_4$ and their particle size depend on the calcination temperature. Calcination temperature also affects the specific surface area and pore volume. The nanocrystalline zinc aluminate was characterized by powder X-ray diffraction, FT-IR spectroscopy, thermal gravimetric analysis, diffuse reflectance spectroscopy, surface area measurements, field emission scanning electron microscopy coupled with energy dispersive X-ray analysis and transmission electron microscopy. Catalytic reactivity of nanocrystalline zinc aluminate was tested for the reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$.

Keywords: A. Sol–gel processes; B. X-ray methods; D. Spinels; Catalytic reactivity

1. Introduction

Nanocrystalline zinc aluminate with spinel type structure is widely applied in various fields because of its interesting properties such as high mechanical strength, high thermal stability, low surface acidity, better diffusion, low temperature sintering ability, wide band-gap energy, hydrophobicity, excellent optical transparency, good metal dispersion capacity and chemical resistance [1–5]. Nanosized zinc aluminate powders and their compact crystal structure are generally used as high temperature ceramic materials, sensors, electronic materials, catalyst and catalytic support of transition metal due to their high specific surface area [6–8]. It has also been used as a heterogeneous catalyst in many reactions, such as acetylation, methylation, dehydration, hydrogenation, dehydrogenation and oxidation of benzyl alcohol to benzaldehyde [6,8–11]. Zinc aluminate nanoparticles are also good photocatalysts, e.g., in the degradation of textile dye and gaseous toluene [12,13]. Zinc aluminate ($ZnAl_2O_4$) is a typical example of normal spinel type structure having the general formula AB_2O_4, where A and B are divalent and trivalent metal ions. In this structure there are four octahedral holes and eight tetrahedral holes per molecule. In normal spinels, A^{2+} ions occupy tetrahedral holes and B^{3+} ions are present in the octahedral holes and the anions are arranged in a cubic close packed array [14].

$ZnAl_2O_4$ nanocrystalline powder has been synthesized by many methods such as microwave assisted hydrothermal [1], co-precipitation [9], hydrothermal [15], solvothermal [16], combustion [17], polymeric precursors [18], modified citrate [19], pyrolysis [20], microemulsion [21], solid state high temperature reactions [22] and evaporation-induced self assembly method [23]. These methods need sophisticated apparatus and are expensive. The major disadvantages of the high temperature, co-precipitation and other methods are that the products obtained usually possess low surface area and inhomogeneity. The significance of the sol–gel process as compared to other methods is that it includes the ability of maintaining a high degree of purity and high homogeneity. Samples are prepared at low temperatures at low cost with good control of size, structure, and morphology [5,11,14]. The sol–gel method has been used to synthesize $ZnAl_2O_4$

*Corresponding author. Tel.: +91 0542 6702879; fax: +91 5422368428.
E-mail addresses: ravikant.iitr.32@gmail.com (R.K. Sharma), rghose.apc@itbhu.ac.in (R. Ghose).

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nanoparticles by several authors. Charinpanitkul et al. [2] and Wei and Chen [3] have reported the preparation of $ZnAl_2O_4$ nanoparticles using ethylacetoacetate and oxalic acid as the chelating agent respectively. In the present work, very pure $ZnAl_2O_4$ nanoparticles have been synthesized without using any chelating agent.

2. Experimental

Aluminium isopropoxide (98%, ALDRICH®), zinc acetate (SRL®), toluene (RANKEM®), ammonia solution (25%, RANKEM®)), 4-nitrophenol (SRL®), $NaBH_4$ (HIMEDIA®), ethanol (MERCK®), and Millipore® water were used as the reagents as received. In the present study, $ZnAl_2O_4$ nanoparticles were synthesized using suitable precursors by the sol–gel method [24]. The details of procedure are as follows.

Zinc acetate: Aluminium isopropoxide (1:2 M ratio), 100 mL of toluene, 40 mL of ethanol and 0.5 mL water (Millipore®) were taken in a 250 mL round bottom flask. The contents were vigorously stirred for 3 h at room temperature till the mixture became homogenous. Then, 2 mL of 25% ammonia solution was added followed by the addition of about 1 mL of water after 1 h. The contents were kept for constant stirring for about 24 h at room temperature (25 °C). The obtained slurry was evaporated at 80 °C to form a gel. The gel was dried at ~80 °C for a few hours and then ground to obtain the xerogel powder. Then the as-prepared powder was calcined in air at 500°, 600° and 700 °C for 3 h inside a muffle furnace (Nabertherm®) to obtain $ZnAl_2O_4$ powder.

Powder XRD patterns were recorded using a Brucker AXS D8 diffractometer operating with Cu-Kα radiation ($\lambda = 0.15406$ nm) with a scanning speed of 2°/min. Thermal gravimetric measurements were carried out in the temperature range 25–1000 °C using a Perkin Elmer (Pyris Diamond) instrument in nitrogen atmosphere at a heating rate of 5°/min. A Thermo Nicolet Nexus Fourier FT-IR spectrophotometer in the range 4000–400 cm^{-1} was used for recording IR spectra of the nanocrystalline powder using KBr disk method. Diffuse reflectance spectra were recorded using a Shimadzu UV-2450 UV-visible spectrophotometer attached with a diffuse reflectance accessory in the wavelength range 200–800 nm using $BaSO_4$ as the reference. The specific surface area of the nanocrystalline powder was measured using Brunauer–Emmett–Teller (BET) method by Micromeritics Chemisorb 2720 instrument using nitrogen physisorption. Morphology of the samples along with elemental analysis (EDXA) data were obtained with a field emission scanning electron microscope (FE-SEM) using FEI Quanta 200 F operating at an accelerating voltage of 20 kV. TEM images of the nanocrystalline powder were recorded using a FEI TECNAI G2 electron microscope operating at an accelerating voltage of 200 kV. The nanocrystalline zinc aluminate powder was dispersed in ethanol using low power sonicator and putting a drop over carbon coated copper grid followed by drying for the TEM measurements.

The catalytic reactivity of the synthesized nanocrystalline zinc aluminate powder was tested by carrying out the conversion of 4-nitrophenol to 4-aminophenol using $NaBH_4$ as the reducing agent at room temperature [20]. This reaction has also been used to find the catalytic activity of different metal aluminate nanoparticles [20,24]. Approximately 50 mL aqueous solution of 4-nitrophenol (0.1 mmol) and 50 mL of freshly prepared aqueous solution of $NaBH_4$ (0.53 mol/L) were taken in a 250 mL beaker. Then, 18.3 mg of the catalyst (zinc aluminate nanoparticles) was added to the above mixture with constant stirring at room temperature. Complete reduction of 4-nitrophenol (yellow colored solution) to 4-aminophenol was indicated by decolorization of the solution and the time taken for the decolorization was noted.

3. Results and discussion

The powder XRD patterns of as-prepared and calcined zinc aluminate powder samples are shown in Fig. 1. The as-prepared sample is X-ray amorphous. It is observed that with increasing temperature crystallinity of the particles increases and also the intensity of the diffraction peaks increases showing that the particle size becomes larger. The powder sample, when calcined at 700 °C gives high intensity fine peaks. The calcined samples show peaks at $2\theta \approx 31.36°$, 36.73°, 44.85°, 49.09°, 55.77°, 59.52°, 65.39°, 74.19°, and 77.35° which are indexed as (220), (311), (400), (331), (422), (511), (440), (620), and (533) diffraction lines showing cubic crystalline zinc aluminate spinel type structure (JCPDS file no. 05-0669). The XRD patterns confirm that the material obtained in the present work is of very high purity with single-phase. The crystallite size of pure nanocrystalline zinc aluminate was calculated using the Debye–Scherrer formula as given below [25].

$$\delta = 0.89\lambda/\beta \cos \theta \quad (1)$$

Where δ is the crystallite size in nm. 0.89 represents a dimensionless constant k, λ is the wavelength of Cu-Kα (0.15406 nm), β is full width at half maxima and θ is the angle. The crystallite size calculated using the most intense peak (311) at $2\theta \approx 36.73°$ of nanocrystalline zinc aluminate calcined at 500° C, 600° C and 700 °C was 3.85 nm, 13.24 nm and 16.80 nm, respectively.

The thermal gravimetric analysis patterns for as-prepared powder show three steps of weight loss (Fig. 2). The first

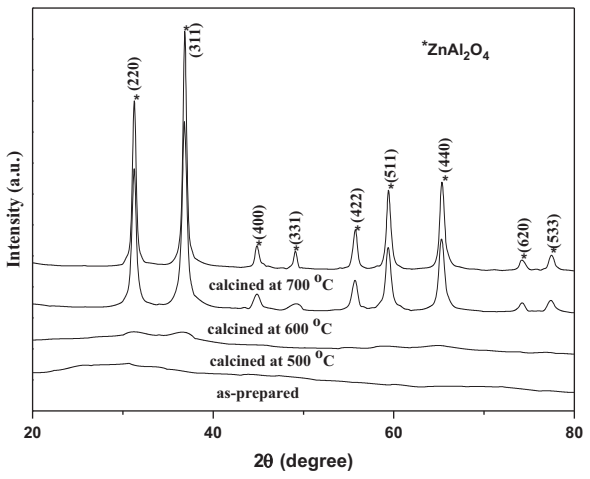

Fig. 1. XRD patterns of nanocrystalline zinc aluminate (before and after calcination).