Comparison of catalytic activity of bismuth substituted cobalt ferrite nanoparticles synthesized by combustion and co-precipitation method

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ABSTRACT

In this study, cobalt ferrite and bismuth substituted cobalt ferrite ($CoFe_{2-x}Bi_xO_4$ $x = 0, 0.1$) nanoparticles were synthesized by two different methods viz combustion and co-precipitation. The nanoparticles were characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), diffuse reflectance spectroscopy (DRS), scanning electron microscopy-energy dispersive X-ray analyzer (SEM-EDX) and vibrating sample magnetometer (VSM). The results of powder XRD pattern showed an increase in lattice parameter and decrease in particle size of cobalt ferrite by the substitution of bismuth. Catalytic activity of cobalt ferrite and bismuth substituted cobalt ferrite nanoparticles synthesized by two different methods were compared for the reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$ as a reducing agent.

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) belongs to the spinel oxide family. It exhibits face-centered cubic structure in which every unit cell containing 32 O^{2-}, 8 Co^{2+} and Fe^{3+} ions. The lattice of oxygen ions are distributed with 64 tetrahedral, 32 octahedral and 24 cations. The eight Co^{2+} and eight Fe^{3+} cations occupy half of the octahedral sites and other eight Fe^{3+} ions occupy eight of the 64 tetrahedral sites, therefore $CoFe_2O_4$ is an example for an inverse spinel structure [1,2]. The $CoFe_2O_4$ nanoparticles are applied in various fields such as data storage [3], magneto-optical devices [4], catalysis [5], biomedical application like drug delivery [6], magnetic resonance imaging [7], biosensor [8] and hyperthermia [9]. $CoFe_2O_4$ is a known hard magnetic material with high coercivity (H_C) and moderate magnetization (M_s) [10].

In recent years there is a swift increase in the pollution level due to textile, paper and pulp, printing, iron-steel, petroleum, pesticides, paint and pharmaceutical industries. The excessive existence of organic pollutant such as synthetic dyestuff, benzene hydrocarbons, sulfonamides, polychlorinated biphenyls (PCBs), phthalates; phenols and aromatic nitro compounds causes serious health hazardous due to their toxic and carcinogenic nature [11]. Among these pollutants, nitrophenols are considered as the major pollutant and occur as contaminants of industrial effluents [12].

4-nitrophenol (4-NP) and its derivatives are extensively used in the production of fungicides, pesticides, herbicides, insecticides, rubbers and synthetic dyes [13]. According to the United states Environmental Protection Agency, the recommended level of 4-nitrophenol in the natural water is 1 μg/L. Therefore degradation and detoxification of 4-nitrophenol is necessary [12,14]. Several treatment processes are available for the removal of nitrophenols such as chemical, physical and biological process. The physical and biological methods have their own demerits such as cost effective, membrane fouling, electrokinetic coagulation, accumulation of concentrated sludge, sludge disposable problems, formation of secondary pollution. Among the several reported methods, reduction of nitrophenols by $NaBH_4$ has emerged as an advantageous method in recent years. The reduction of 4-nitrophenol using $NaBH_4$ will be enhanced in terms of time and percentage of conversion using the catalyst [11,12,15]. There by a suitable catalyst is required to facilitate the reduction of 4-nitrophenol.

So far there are only less number of reports are available on ferrites in the catalytic reduction of 4-nitrophenol. This encourages us to shed light on the synthesis of cobalt ferrite and bismuth substituted cobalt ferrite and to study its catalytic activity for the reduction of 4-nitrophenol. Cobalt ferrites are synthesized by several methods such as sol–gel [16], hydrothermal [17], combustion [18], co-precipitation [19], thermal decomposition [20] and micro emulsion [21]. Among these methods, combustion reaction paves a simple and quick way of ferrite synthesis. The major advantages are short preparation time, high purity, crystallinity,

good chemical homogeneity and simple procedure [18]. Similarly, co-precipitation methods also have advantages of homogeneity, small particle size, high porosity and purity, low temperature preparation and simple process [22]. Cobalt ferrite exhibits good catalytic activity too [23]. Bismuth and its substituted compounds are being used in various fields such as development of cosmetic products, lubricating oils, medicines, pigments, electronics, semiconductors, alloys industry and recycling of uranium nuclear fuels [24–27]. In recent years, bismuth substituted nickel ferrite and cobalt ferrite compounds are reported for magnetic and dielectric properties [16,28]. To the best of our knowledge bismuth substituted cobalt ferrite nanoparticles are not explored for the reduction of 4-nitrophenol.

In this present work, cobalt ferrite and bismuth substituted cobalt ferrite ($CoFe_{2-x}Bi_xO_4$ $x=0$, 0.1) nanoparticles are synthesized by two different methods viz combustion and co-precipitation. The catalytic activity of cobalt ferrite and bismuth substituted cobalt ferrite nanoparticles are compared for the first time in the reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$ as reducing agent in aqueous medium at room temperature.

2. Experimental

2.1. Materials

Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, s.d fine 97.0%), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, HIMEDIA 98.0%), bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, s. d fine 98.5%), glycine ($C_2H_5NO_2$, s.d fine 99.5%), ammonia solution, 4-Nitrophenol (Avra 99%) and $NaBH_4$ (Avra 98%).

2.2. Methods

2.2.1. Combustion

Cobalt ferrite and bismuth substituted cobalt ferrite $CoFe_{2-x}Bi_xO_4$ ($x=0$, 0.1) nanoparticles were synthesized by solution combustion method using glycine as a fuel. The aqueous solution of $Co(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ were prepared and known quantity of glycine was added as a fuel to the mixed precursors and they were concentrated in a beaker on a hot plate at 60 °C for 10–15 min. After that the mixture was allowed to undergo the spontaneous combustion at 500 °C in the furnace. The mixture began burning and all the solutions vaporized instantly, resulting in the formation of a brown voluminous and fluffy ferrite product. The acquired substance ground into fine powder and sintered at 700 °C for 2 h.

2.2.2. Co-precipitation

Cobalt ferrite and bismuth substituted cobalt ferrite ($CoFe_{2-x}Bi_xO_4$ $x=0$, 0.1) nanoparticles were prepared by co-precipitation method. The details of the procedure is as follows: stoichiometric amount of $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ were weighed and dissolved in 15 ml of double distilled water and stirred for 10 min. The aqueous ammonia was added to the mixture of the solution to maintain the pH value 10.5. After 30 min stirring, the precipitated slurry was filtered and washed several times with distilled water and dried at 70 °C for 24 h. The obtained powder was treated at 750 °C for 8 h.

2.3. Catalytic activity

The catalytic activity of the synthesized compounds were tested in the reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$ as reducing agent [29]. Approximately 5 ml aqueous solution of 4-nitrophenol (0.1 mmol) and 12.5 ml of freshly prepared aqueous solution of $NaBH_4$ (0.53 mol) were taken in a 100 ml beaker. Then, 25 mg of the cobalt ferrite or bismuth substituted cobalt ferrite catalyst were added and stirred at room temperature. The complete reduction of 4-nitrophenol (yellow color solution) to 4-aminophenol was indicated by decolorization of the solution. The time taken for the decolorization was noted. The conversion of 4-nitrophenol to 4-aminophenol was confirmed by UV–visible spectroscopy.

2.4. Characterization

The compound was characterized by powder X-ray diffraction (XRD) (D8 advance BRUKER Germany) in the 2 theta range $10-70°$. Fourier transforms infrared spectrophotometer (FT-IR) was recorded in the range 2500–400 cm^{-1} using FT-IR SHIMADZU model. Optical properties of the compounds were analysed using diffuse reflectance spectroscopy (DRS) (JASCO-V670 spectrophotometer) and surface morphology of the synthesized compounds was analysed using ZESIS EVO18 SEM instrument. The magnetic properties were measured at room temperature by a vibrating sample magnetometer (Lakeshore VSM 7410). Reduction of 4-nitrophenols was analysed using UV–Visible spectrometer (HITACHI, 2542-004).

3. Results and discussion

3.1. Powder XRD analysis

The powder XRD pattern of cobalt ferrite and bismuth substituted cobalt ferrite ($CoFe_{2-x}Bi_xO_4$ $x=0$, 0.1) nanoparticles prepared by combustion and co-precipitation methods are shown in Fig. 1(a) and (b). All peaks corresponding to the (111), (202), (311), (222), (400), (422), (333) and (404) planes indicate the presence of single phase cubic structure according as JCPDS card no. 96-591-0064. The lattice parameter is calculated using the formula given below [30]

$$a = d\left[\left(h^2 + k^2 + l^2 \right) \right]^{1/2}$$

where, h, k and l are miller indices, d- inter planar distance and a-lattice parameter.

The average crystallite size of pure cobalt ferrite and bismuth substituted cobalt ferrite nanoparticles are calculated using the Scherrer's formula [30]

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where, D is the average crystalline size, λ is the X-ray wavelength, β is the full-width at half maximum (FWHM) and θ is the Bragg's angle. The lattice parameter and average crystalline size are calculated and given in Table 1. It is observed that the lattice parameter of cobalt ferrite increases and the average crystalline size of the cobalt ferrite decreases when bismuth ion is substituted irrespective of the method of synthesis. This could be due to the large ionic radii of Bi^{3+} (1.03 Å) [24] than Fe^{3+} (0.64 Å) [28]. Bi^{3+} has a strong site preference for the B-site (octahedral site). Therefore, the replacement of Fe^{3+} by Bi^{3+} resulted in the expansion of unit cells. Similar observation is noted by Panda et al. [28].

3.2. FTIR analysis

FT-IR spectra of cobalt ferrite nanoparticles found to exhibit two major bands in the range 400–700 cm^{-1} as shown in Fig. 2 (a) and (b). The spectrum of nanoparticles synthesized by both the methods results in high frequency band (v_1) ranges from 514 to 523 cm^{-1} and lower frequency band (v_2) ranges from 416 to