



Growth of zinc hexacyanoferrate nanocubes and their potential as heterogeneous catalyst for solvent-free oxidation of benzyl alcohol

S.R. Ali^{a,*}, V.K. Bansal^b, A.A. Khan^b, S.K. Jain^c, M.A. Ansari^d

^a Department of Chemistry, Government (P.G.) College, Narayan Nagar 262550, Uttarakhand, India

^b Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India

^c Department of Chemistry, Gurukula Kangri University, Haridwar 249404, Uttarakhand, India

^d Department of Chemistry, Bipin Bihari (P.G.) Science College, Jhansi 284001, U.P., India

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ABSTRACT

Zinc hexacyanoferrate nanocubes have been synthesized following an extremely simple method and characterized by elemental analysis, thermal analysis, infrared spectroscopic and X-ray diffraction techniques. Field emission scanning electron microscopic image showed that it consisted of sharp cubic particles with size ranging from 83 to 164 nm. Catalytic activity of nanocubic zinc hexacyanoferrate has been studied for solvent-free oxidation of benzyl alcohol using H₂O₂ as oxidant under the optimum conditions of certain parameters such as benzyl alcohol to H₂O₂ molar ratio, the amount of catalyst, reaction time and temperature.

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1. Introduction

Owing to their extraordinary size and shape dependant properties, numerous nanomaterials based on various metals and metal complexes have been synthesized and characterized during the past few years. Nanomaterials exhibit severalfold enhanced properties such as magnetic, electrical, optical, surface, chemical, catalytic and biological activities [1–4] due to which these materials show their potential applications in various interdisciplinary areas including biological diagnosis, biomedicine, controlled drug delivery, enzyme immobilization and biosensing [5–9]. Nanomaterials have been proposed for their promising use in advancement of magnetic resonance imaging and magnetic memory devices [10,11]. Nanomaterials are creating a great impact nanocoating, nanofilm and nanostructured surfaces made by several modified techniques [12–14]. Besides these, nanomaterials have their wide scope of interest in academic researches. From the synthetic point of view, one of the important subjects is to prepare well dispersed nanoparticles with well defined shape and uniform size. Recent studies show that controlling the growth of metal coordination polymers under special confinement could be a good methodology for their synthesis in nano form.

Among the coordination complexes of transition metal, metal hexacyanoferrates have been extensively studied due to their outstanding characteristics such as high water insolubility, mixed valency, high ionic conductivity and excellent redox mediator properties [15–17]. Most of the metal hexacyanoferrates possess microporous, polynuclear and open channel structure [18,19]. These complexes do not dissolve upon their oxidation/reduction as their zeolitic structure allows the diffusion of ion in or out maintaining electrical charge neutrality. The above characteristic properties of metal hexacyanoferrates make them much useful in preparation of molecular magnet, photomagnet, ferromagnet, optical device, rechargeable solid state battery, electrochromic device, adsorbent, ion-exchanger and catalyst. Nickel-, copper-, cobalt-, cadmium- and other metal hexacyanoferrates have been proposed as the effective and selective tool for the recovery of valuable metals such as silver as well as for the removal of hazardous cations viz., radioactive cesium, palladium, lead and strontium from the waste water of metallurgical plants [20,21]. Recently, metal hexacyanoferrates have been used as catalyst for the polymerization of ethylene oxide into polymers of commercial importance [22–24]. Catalytic activities of certain metal hexacyanoferrates towards the oxidation of cystien, aniline and anisidine have also been studied [25–27]. Kamaluddin and his coworkers have studied the interaction of numerous organic molecules including amino acids, nucleotides and nitrogen bases with metal hexacyanoferrates [28–32]. High electrocatalytic activities of metal hexacyanoferrates open new possibilities in development of electrochemical sensors for the detection of

* Corresponding author. Tel.: +91 9997418110.

E-mail address: shahrajali@gmail.com (S.R. Ali).

various inorganic and organic molecules. Electrochemical sensors based on metal hexacyanoferrate modified electrodes for detection of hydrazine, thiosulfate, nitrate and phosphate have been prepared [33,34]. The utility of metal hexacyanoferrates in sensing the molecules of environmental and biological interest including glucose, ascorbic acid, dopamine, epinephrine, norepinephrine, β -NADPH insulin, morphine and paracetamol drug has also been reported [35–43]. In most of these areas, metal hexacyanoferrates have been employed in their conventional form, as the nanochemistry of these materials has yet not been explored so far. However, few publications are available on the synthesis, characterization of these complexes. Recently, copper and nickel hexacyanoferrate nanoparticles were synthesized and characterized [44,45]. Kong et al. [46] reported the preparation of some transition metal hexacyanoferrates. Syntheses, characterization and catalytic activities of nanoscaled metal hexacyanoferrates are under study in our laboratory. In this paper we describe our results on the growth of zinc hexacyanoferrate nanocubes and their catalytic activity for solvent-free oxidation of benzyl alcohol into benzaldehyde. This reaction is of considerable importance because of benzaldehyde is used as the starting material in the synthesis of odorants, flavors and pharmaceutical intermediates. Different catalysts for this reaction have been reported [47–49].

2. Experimental

2.1. Chemicals

Potassium hexacyanoferrate trihydrate (Merck), zinc nitrate hexahydrate (Merck), potassium chloride (Merck), EDTA (Merck) and benzyl alcohol (Merck) were used as received. All other chemicals were of analytical reagent grade. Doubly distilled water was used throughout the experiment.

2.2. Growth of zinc hexacyanoferrate nanocubes

Zinc hexacyanoferrate nanocubes were synthesized from potassium hexacyanoferrate trihydrate using the double decomposition method adopted by Qu et al. [41]. 100 ml of 0.01 M solution of zinc nitrate containing an equimolar amount of EDTA was slowly added to 50 ml of 0.01 M solution of potassium hexacyanoferrate trihydrate containing an equimolar amount of potassium chloride with constant stirring at room temperature. After complete mixing, the reaction mixture was vigorously agitated for 5 min and then kept as such for 30 min. The aqueous suspension so obtained was filtered on a Buckner funnel, washed thoroughly with water and dried in an oven at about 60 °C overnight. The solid material was then crushed and sieved to a 100 mesh size.

2.3. Characterization of zinc hexacyanoferrate nanocubes

Zinc hexacyanoferrate nanocubes were characterized before and after its use in the oxidation of benzyl alcohol. The percentage of carbon, nitrogen and hydrogen was recorded on an Elementar Vario ELHI CHNS analyzer. Zinc and iron percentages were determined using a Perkin Elmer atomic absorption spectrophotometer. Data of the elemental analysis is shown in Table 1. Thermogram for thermogravimetric and differential thermal analysis of zinc

Table 1
Elemental analyses and TG/DT analyses of nanocubic zinc hexacyanoferrate.

	C (%)	N (%)	H (%)	Zn (%)	Fe (%)
Theoretical values	18.12	21.14	1.51	33.07	14.09
Observed values	18.34	20.87	1.66	33.23	13.89
Recycled catalyst values	17.98	20.93	1.61	32.86	13.94

Table 2
X-ray diffraction data of nanocubic zinc hexacyanoferrate.

S. No.	<i>d</i> (Å)	<i>I</i> / <i>I</i> ⁰
1	5.41 (5.40)	90 (88)
2	4.51 (4.51)	34 (35)
3	4.09 (4.08)	100 (100)
4	3.64 (3.64)	38 (40)
5	3.11 (3.11)	29 (30)
6	2.69 (2.70)	22 (20)
7	2.54 (2.54)	21 (20)

Values in parentheses indicate reported data.

hexacyanoferrate nanocubes was recorded on a Perkin Elmer analyzer system (Pyris Diamond). The heating rate was 10 °C/min. All measurements were carried out in air atmosphere using Al₂O₃ as reference. The thermogravimetric and differential thermal spectra showed 13.9% and 13.8% mass loss, before and after the use of zinc hexacyanoferrate nanocubes in oxidation of benzyl alcohol, respectively. These values are nearly the same as the theoretical values (13.6%) calculated for three water molecules in the molecular formula of synthesized nanocubic zinc hexacyanoferrate. Infrared spectra of the synthesized nanocubes were recorded in KBr disc on a Perkin Elmer spectrophotometer. X-ray diffraction analysis of nanocubic zinc hexacyanoferrate was carried out using a Philips PW-1140/90 X-ray diffractometer. The relative-intensity data and interplanar spacing (*d*) values were found nearly the same as the reported values. The data is shown in Table 2. Surface morphology and particle size of the complex was studied using a Quanta 200 FE-SEM instrument. FE-SEM image of nanocubic zinc hexacyanoferrate is shown in Fig. 1.

2.4. Catalytic activity measurements

Catalytic activity of zinc hexacyanoferrate nanocubes was studied for solvent free oxidation of benzyl alcohol using H₂O₂ as oxidizing agent. The effect of reaction conditions, namely, benzyl alcohol to H₂O₂ molar ratio, the amount of catalyst, reaction time and temperature was studied to optimize the reaction parameters for which the reaction was performed by changing one of the parameters and keeping others constant. The reaction was carried out in a magnetically stirred round bottom flask (25 cm³) fitted with a mercury thermometer and a reflux condenser. To determine the percent conversion of benzyl alcohol, small aliquot of reaction mixture was withdrawn periodically and centrifuged to remove the catalyst. Reaction of 50 mmol of benzyl alcohol with 100 mmol of

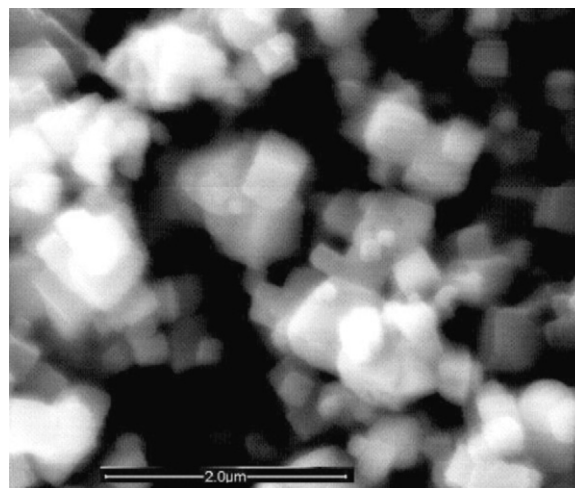


Fig. 1. FE-SEM image of zinc hexacyanoferrate nanocubes.

H₂O₂ (30%) in the presence of 30 mg catalyst at 75 °C showed maximum progress of reaction within 3 h. The catalyst-free reaction mixture so obtained was then subjected to the quantitative analysis using a Thermolectron gas-chromatograph with an HP-I capillary column (30 m × 0.25 mm × 0.25 μm) and an FID detector. The catalyst removed from the reaction mixture was washed thoroughly with water, dried, and then characterized again to confirm that the composition and structure of catalyst remain unchanged after the reaction.

3. Results and discussion

3.1. Growth of zinc hexacyanoferrate nanocubes

Synthesis of zinc hexacyanoferrate nanocubes is very simple. On mixing the solution of zinc ions with the solution of hexacyanoferrate ions, the growth of zinc hexacyanoferrate nanocubes takes place. It seems that the addition of EDTA during the course of reaction facilitates the formation of zinc hexacyanoferrate nanoparticles with almost uniform shape and definite size range (63–164 nm) as proposed by Qu et al. [41]. Formation of zinc complexes with EDTA decreases the effective concentration of zinc ions, which results in the homogenous precipitation forming zinc hexacyanoferrate nanocubes of the size range mentioned above [50].

The composition of zinc hexacyanoferrate nanocubes was determined by CHNS analysis, atomic absorption spectroscopy and TG/DT analysis. The results revealed the molecular formula of synthesized zinc hexacyanoferrate as Zn₂[Fe(CN)₆]·3H₂O. These zinc hexacyanoferrate nanocubes were examined by X-ray diffraction measurements and the data are presented in Table 2. It confirms that all the diffraction peaks can be indexed to the cubic structure of zinc hexacyanoferrate. Interplanar spacing and the relative intensity data were found in good agreement with the reported values. The clear and sharp X-ray peaks indicated the high crystallinity of synthesized nanomaterial. Infrared spectral studies of zinc hexacyanoferrate nanocubes showed a strong peak at 2080 cm⁻¹ corresponding to the characteristic peak of the C≡N group present in -Fe(II)-CN-Zn(II)- species. It shows that both zinc and iron in synthesized complex exist in their divalent oxidation state. These results are consistent with its molecular formula deduced from elemental and TG/DT analyses. The FE-SEM image (Fig. 1) indicates that the synthesized nanocubic zinc hexacyanoferrate consists of the particles with uniform cubic shape. Its morphology was clear and well dispersed with sharp nanocubes. However, slightly agglomerated particles were observed during its morphological investigations. Zinc hexacyanoferrate nanocubes with size ranging from 83 to 164 nm were observed.

For the hexacyanoferrates of divalent transition metal ions, the general molecular formula M₂[Fe(CN)₆]·nH₂O has been reported, where M represents an exchangeable transition metal and n represents the number of water molecules present in the interstitial site of the lattice [51]. The species [Fe(CN)₆]⁴⁻ in zinc hexacyanoferrate exist in octahedral geometry where the central iron is surrounded by six CN⁻ ligands and has the electronic configuration t_{2g}⁶. Although the CN⁻ ligand is bonded to Fe through σ donation, there is sufficient back bonding from dπ orbital of iron to antibonding pπ orbital of CN⁻ ligand. In a structural aspect, Prussian blue is one of most studied metal hexacyanoferrate. The face-centered cubic lattice structure of Prussian blue is a characteristic of many other transition metal hexacyanoferrates. Shriver has studied the systematics of the lattice parameters for Prussian blue analogues [52]. The transition metal hexacyanoferrates generally have polymeric lattice structure with repetition of [Fe(CN)₆]⁴⁻ anions, in which outer transition metal ions are coordinated with the nitrogen atom of cyanide ligand. Detailed

structural study of Prussian blue and related complexes was carried out by Ludi and Gudel [53]. Recently, Reguera and coworkers have studied the structural behavior of some metal hexacyanoferrates [54–56].

3.2. Catalytic studies

The catalytic oxidation of benzyl alcohol was studied using H₂O₂ as oxidant and zinc hexacyanoferrate nanocubes as heterogeneous catalyst in the absence of any solvent. Generally, benzyl alcohol oxidizes into benzaldehyde, benzoic acid and benzyl benzoate. However, only benzaldehyde was characterized as the oxidation product in the present case. Blank reaction performed over zinc hexacyanoferrate nanocubes under the same reaction conditions showed negligible conversion of benzyl alcohol into benzaldehyde. In the absence of catalyst, no significant amount of benzaldehyde was produced indicating that H₂O₂ alone is unable to oxidize benzyl alcohol into benzaldehyde. Under the optimum reaction conditions, nearly 28% conversion with 100% selectivity was recorded. No significant change in elemental analysis, TG/DT analysis and X-ray diffraction data of zinc hexacyanoferrate nanocubes before and after its use in the present reaction indicated that its composition and structure do not change after its involvement in the reaction. Thus it was confirmed that zinc hexacyanoferrate nanocubes participated in the reaction as a catalyst rather than a reactant.

3.2.1. Effect of H₂O₂ concentration

The effect of the amount of H₂O₂ oxidant on the oxidation of benzyl alcohol into benzaldehyde was studied and the results are shown in Fig. 2a. The percent conversion of benzyl alcohol into benzaldehyde is dependent upon the amount of H₂O₂ up to a considerable extent. The amount of H₂O₂ was varied in terms of benzyl alcohol to H₂O₂ molar ratio. Benzyl alcohol to H₂O₂ molar ratio of 1: 1 resulted in 19.9% conversion when the amount of catalyst was 30 mg, temperature was 75 °C and reaction time was 3 h. When benzyl alcohol to H₂O₂ molar ratio was raised to 1:2, the conversion increased up to nearly 28% under all other similar conditions. However, the conversion was found almost constant (28.1% and 28.2%) when benzyl alcohol to H₂O₂ molar ratio was further increased up to 1:3 and 1:4. Therefore, 1:2 molar ratio for benzyl alcohol and H₂O₂ was found the optimum ratio. Oxygen produced on the decomposition of H₂O₂ oxidizes benzyl alcohol. When benzyl alcohol:H₂O₂ ratio was 1:1, the conversion of benzyl alcohol was low, which may be due to insufficiently available oxygen. It seems that the amount of oxygen required to react with the whole fraction of active molecule of benzyl alcohol was sufficiently produced in the case of benzyl alcohol to H₂O₂ molar ratio of 1:2. Oxygen produced in the case of benzyl alcohol to H₂O₂ molar ratio of 1:3 and 1:4 may be more than that of its minimum amount required to react with the whole fraction of active molecule of benzyl alcohol.

3.2.2. Effect of catalyst concentration

Effect of the amount of catalyst upon the oxidation of benzyl alcohol was studied by varying its amount from 10 to 40 mg with all other reaction parameters fixed, namely, temperature (75 °C), benzyl alcohol to H₂O₂ molar ratio (1:2) and reaction time (3 h). The results are shown in Fig. 2b, indicating 20.1, 25.4, 28.1 and 28.2% conversion corresponding to 10, 20, 30 and 40 mg catalyst, respectively. Lower conversion of benzyl alcohol into benzaldehyde with 10 and 20 mg catalyst may be due to fewer catalytic sites.

The maximum reaction progress was observed with 40 mg catalyst but there was no remarkable difference in the progress of reaction when 30 and 40 mg catalyst was employed. Therefore, the optimum amount of catalyst was 30 mg.

3.2.3. Effect of temperature

The influence of temperature on the oxidation of benzyl alcohol was investigated by performing the reaction at a temperature range from 45 to 90 °C with all other parameters fixed (reaction time, 3 h; benzyl alcohol to H₂O₂ ratio, 1:2 and catalyst 30 g). The results are given in Fig. 2c, which reveals that the conversion is dependant on temperature. 11.7%, 22.9%, 28.2% and 28.2% conversion was recorded corresponding to 45, 60, 75 and 90 °C. Therefore, temperature of 75 °C was selected as the optimum condition. At lower

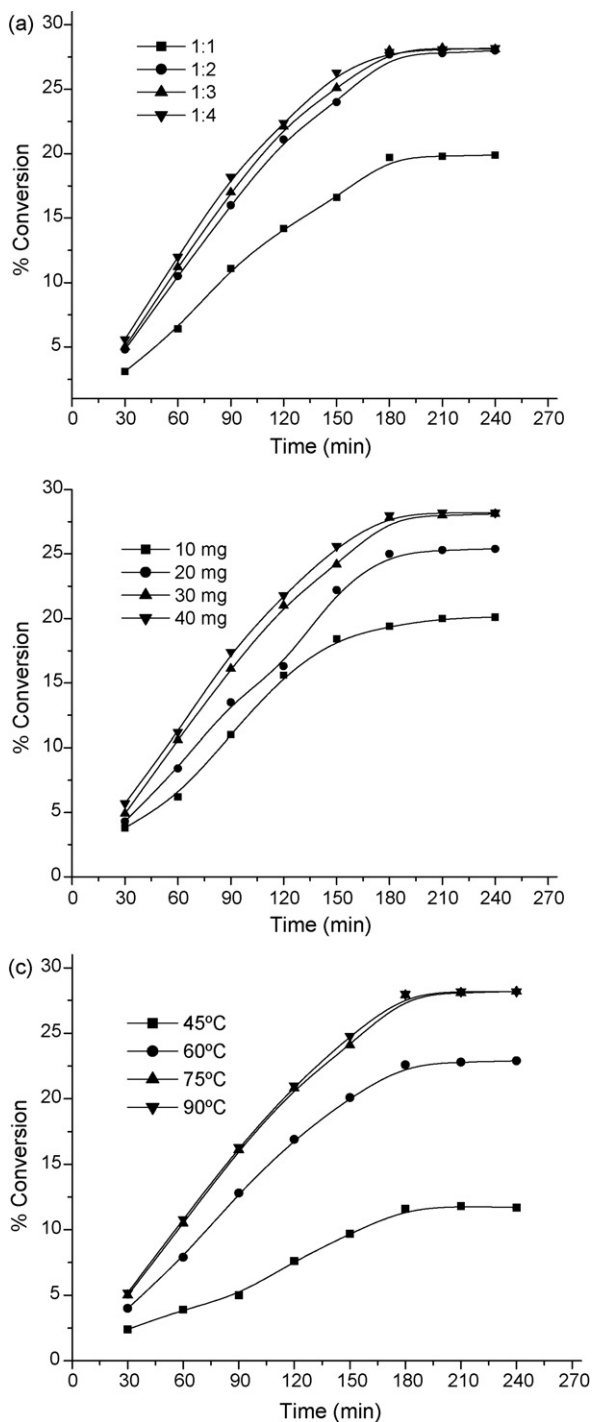


Fig. 2. (a) Effect of benzyl alcohol to H₂O₂ molar ratio (75 °C temperature, 30 mg catalyst, 3 h time). (b) Effect of the amount of catalyst (75 °C temperature, 1:2 ratio of benzyl alcohol to H₂O₂, 3 h time). (c) Effect of temperature (75 °C temperature, 30 mg catalyst, 1:2 ratio of benzyl alcohol to H₂O₂, 3 h time).

temperature, the conversion of benzyl alcohol into benzaldehyde was considerably decreased.

3.2.4. Effect of reaction time

The time dependence of the catalytic solvent-free oxidation of benzyl alcohol into benzaldehyde was studied by performing the reaction of 50 mmol benzyl alcohol with 100 mmol of 30% H₂O₂ in presence of 30 g of catalyst at 75 °C with constant stirring. The percentage of conversion was monitored at different reaction times and the results are shown in Fig. 2a–c, which reveal that the initially the reaction rate is low and increases up to 3 h. There is no significant increase in the conversion of benzyl alcohol into benzaldehyde even the reaction time was increased up to 4 h.

4. Conclusion

Zinc hexacyanoferrate nanocubes can be synthesized by mixing the solution of zinc ions with the solution of hexacyanoferrate ions. The addition of EDTA leads to the zinc hexacyanoferrate nanoparticles with the uniform shape and a definite size range. The synthesized zinc hexacyanoferrate nanocubes act as heterogeneous catalyst for the solvent-free oxidation of benzyl alcohol into benzaldehyde. Under optimized conditions, the conversion was nearly 28%.

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