



Comparative studies of synthesis of nanosized ferrite from the thermolysis of di-and tri-phenylamine substituted pentacyanoferrate complexes

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ABSTRACT

Ferrite material has been under intense research for so long due to their useful electromagnetic characteristics for large number of applications. Magnetic nanoparticles have attracted paramount interest in past few years not only because of their application in magnetic recording, information storing, data processing devices and magnetic resonance imaging and drug delivery systems but also in fundamental physics. At present study thermal analysis of di and triphenylamine substituted pentacyanoferrate (II), $Na_3[Fe(CN)_5L] \cdot xH_2O$ where L= di and triphenylamine complexes has been carried out in flowing air atmosphere from ambient temperature to 900 °C. Various physicochemical techniques i.e. TGA-DTG, IR, XRD and Mössbauer spectroscopy have been carried out to characterize the intermediate, end products and nanostructured materials. Mössbauer spectra of these complexes exhibits quadrupole doublet with $(\Delta E_Q) = 0.69-0.71 \text{ mms}^{-1}$ at room temperature and isomer shift $(\delta) = 0.01 \pm 0.03 \text{ mms}^{-1}$ suggests that the iron atom is in the = +2 low spin state. Thermogram of di and diphenylamine substituted complexes show multistage decomposition. The complexes start decomposing at 50°C yielding residual weight 21.6 and 18.9 % at temperature $\sim 985 \pm 5 \text{ }^\circ\text{C}$. The Mössbauer spectra recorded after heating at 300°C exhibit single line suggesting partial decomposition. At 500 and 750 °C, six lines pattern start appearing which on further heating at 950 °C turns into four sextet suggesting the formation of mixture $Fe_3O_4(A)$, $Fe_3O_4(B)$, Fe_3C and $\alpha\text{-}Fe_2O_3$. The temperature of ferrite formation is much lower than possible in the conventional ceramic method.

Keywords: Mössbauer spectroscopy, pentacyanoferrate, ferrites

INTRODUCTION

The need of high resistivity ferrites led to the synthesis of their magnetic materials by various techniques[1]. Superparamagnetic iron oxide nanocrystals have been found application in different fields, from e.g. magnetic recording media to cancer treatment by hyperthermia[2]. Earlier we have studied several alkyl and aryl amine substituted pentacyanoferrate(II) complexes[3-5]. Coelho et[6] has been given special attention to the study of interaction of iron with ligand of biological importance, therefore, thermal behavior of simple and complex cyanide has been the subject matter of much work. Also ferrites formed at higher temperature are widely employed in industry as catalysts and ferromagnetic materials[7]. Brar and Varma[8] studied thermal decomposition product of sodium pentacyanoferrate(II) using Mössbauer spectroscopy. Sielo et al[9] have reported the thermal behavior of pentacyanoferrate(II) complexes with L= pyrazine and pyridine and proposed the water release and finally yield metal carbide. In the present study, we prepared fine particles of iron oxides by using thermal decomposition to confirm the differences in the particle size and chemical state of iron oxides. In order to characterize, their Mössbauer spectroscopy, TGA, DTA and IR were used.

MATERIALS AND METHODS

Preparation of substituted pentacyanoferrate (II) complexes

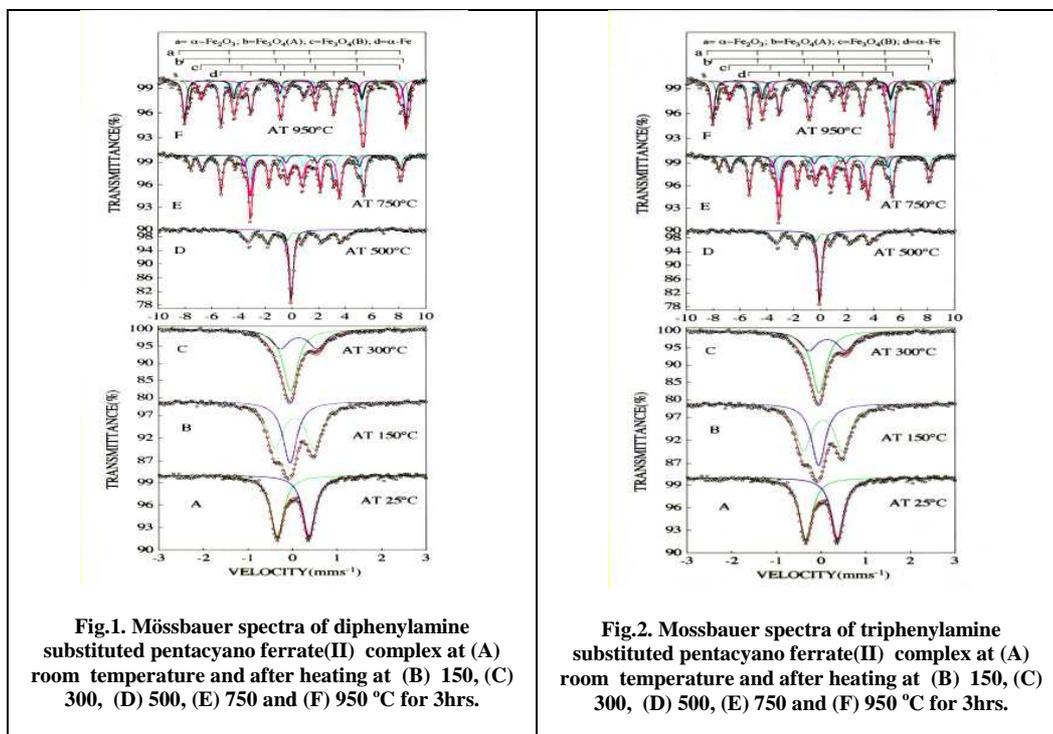
A solution containing 0.47g of hydroxylamine hydrochloride and 0.54g NaOH in 20 mL water was prepared. Then 10% ligand (L= diphenylamine and triphenylamine) ethanol was added. The mixture was kept in ice for 1hr and then added dropwise to an ice cold solution of 2g sodium pentacyanonitrosylferrate(II) in 20mL water. In each case an oily layer separated after adding cold alcohol. The complexes were forced to solidify by through washing with absolute ethanol and then drying for 24hr over concentrated sulphuric acid in desiccator.

Physical measurements

Infrared spectra in KBr medium were recorded on an FTIR (HITACHI Nicolet) spectrophotometer. The Mössbauer spectra were recorded on transducer driven Mössbauer spectrometer in constant acceleration mode (ELCENT) at room temperature. A ~5 mCi $^{57}\text{Co}(\text{Rh})$ source was used. The spectrometer was calibrated using a natural iron foil. The isomer shift values were reported with respect to metallic iron. The spectra were fitted with Lorentzian line shapes by using least square fitting procedure. UV-visible spectra of the substituted pentacyanoferrate(II) complexes were recorded in aqueous solution using Hitachi Model U-3500 spectrophotometer and 1cm path length. Infrared spectra were obtained on a sample in KBr pallets using Hitachi Nicolet Model-I 5040 FTIR spectrophotometer. The thermogravimetric (TGA-DTA) were carried out using Seiko Instrument Inc.SSC/5200. XRD of decomposition products were recorded using MAC science MXP-18 automated diffractometer by Cu-K α radiation.

RESULTS AND DISCUSSION

The complexes are coloured solid and stable under normal atmospheric conditions. ^{57}Fe Mössbauer spectra of all the complexes exhibit a well resolved quadrupole doublet at room temperature. Typical Mössbauer spectra of di and triphenylamine substituted pentacyanoferrate(II) complexes at room temperature and after heating at different temperatures are shown in Fig.1 and Fig.2. The Mössbauer parameters such as isomer shift (IS) and quadrupole splitting (ΔE_Q) derived from the observed spectra are summarized in Table 2. The spectra consist of one doublet with small quadrupole splitting (ΔE_Q) is shown in the same Fig.1. The values of IS and QS indicate that the iron atom in this complexes is at Fe(II) low spin state at room temperature.



The ΔE_Q values is 0.74 mms^{-1} . It is observed from Table.1 that isomer shift (δ) values for all the complex at room temperature are within $0.00 \pm 0.02 \text{ mms}^{-1}$ (w.r.t. natural iron) suggesting low spin state of Fe(II) in octahedral geometry[10-12].

The decomposition of these complexes begins at 50°C and the plateau is observed in the temperature range 200 to

475 °C. The complexes undergoes dehydration at this range as shown by an inflexion in the TG curve. DTG also shows a broad peak at 85 °C for triphenylamine complex while there are two DTG peaks are at 75 and 130 °C for diphenylamine complex. The anhydrous compound does not show any arrest in TGA curve and undergoes abrupt mass loss of 17% at 165 °C suggesting the removal of 3-4 water molecules. Mössbauer spectrum obtained of the residue obtained by calcining the parent complex at 150 °C for 3hrs displayed two doublet with singlet for both these complexes. Similar behavior of TGA curve obtained for both the complexes. The weight loss percentage at 200 °C is ~17% which is good agreement with the calculated value by assuming the formation of anhydrate. Further heating causes a slow decomposition upto 750 °C with the loss of ligand and cyanide group and abrupt loss of weight were found in the temperature range 750-980 °C followed by the last plateau.

Table 1. Mössbauer parameters for substituted pentacyanoferrate(II) and its thermal decomposition products

| Complex Na ₃ [Fe(CN) ₅ L] L= | Temp/ °C | Isomer shift, δ , mms ⁻¹ | Quadrupole splitting, ΔE_Q , mms ⁻¹ | H _{eff} / kOe | Possible products |
|--|-------------|---|---|---------------------------|--|
| diphenylamine | 25 | 0.01 | 0.71 | - | - |
| | | 0.04 | 0.87 | - | - |
| | 150 | -0.06 | - | - | - |
| | | 0.15 | 0.83 | - | - |
| | 300 | -0.04 | - | - | - |
| | | 0.20 | -0.01 | 217 | Fe ₃ C |
| | 500 | -0.07 | - | - | - |
| | | 0.25 | -0.04 | 486 | Fe ₃ O ₄ (A) |
| | 750 | 0.71 | 0.01 | 463 | Fe ₃ O ₄ (B) |
| | | 0.00 | 0.01 | 331 | α -Fe |
| | | 0.19 | 0.00 | 207 | Fe ₃ C |
| | | 0.49 | 0.02 | 514 | α -Fe ₂ O ₃ |
| | 950 | 0.30 | 0.16 | 501 | Fe ₃ O ₄ (A) |
| | | 0.61 | -0.05 | 462 | Fe ₃ O ₄ (B) |
| 0.01 | | 0.01 | 332 | α -Fe | |
| | | | | | |
| Triphenylamine | 25 | 0.03 | 0.69 | - | - |
| | | 0.04 | 0.85 | - | - |
| | 150 | -0.06 | - | - | - |
| | | 0.08 | 0.94 | - | - |
| | 300 | -0.06 | - | - | - |
| | | 0.19 | -0.01 | 201 | Fe ₃ C |
| | 500 | -0.06 | - | - | - |
| | | 0.19 | -0.01 | 208 | Fe ₃ C |
| | 750 | -0.06 | - | - | - |
| | | 0.40 | -0.16 | 517 | α -Fe ₂ O ₃ |
| | 950 | 0.26 | 0.03 | 488 | Fe ₃ O ₄ (A) |
| | | 0.70 | 0.11 | 467 | Fe ₃ O ₄ (B) |
| | | 0.04 | 0.00 | 333 | α -Fe |

In order to characterize the decomposition of these complexes in each plateau, Mössbauer and X-ray diffraction were measured at different temperatures. The Mössbauer spectrum of these complexes obtained at 150 °C (Fig.2B, 3B), shows a slight change in the shape of absorption band, but the isomer shift does not change. Only the quadrupole splitting values are increased in both cases. This indicates that decomposition has started. Thermogravimetric analysis indicates the loss of water molecules. Differential analysis shows an endothermic peak at 110 °C which is due to the loss of water molecules. From these fact, it can be concluded that at 150 °C diphenyl an triphenylamine substituted pentacyanoferrates(II) has just started decomposing. The slight change in the shape of Mössbauer spectrum may be due to loss of water molecules.

The Mössbauer spectrum of the diphenyl and triphenylamine substituted complexes, obtained at 300 °C, are different from those at 150 °C. Mössbauer spectra of substituted pentacyanoferrate(II) complex heated at 300 °C for 3 hr exhibit an asymmetric doublet typically shown in Fig.1C which may be further resolved into quadrupole doublet ($\Delta E_Q = 0.83$ and 0.94 mms⁻¹; $\delta = 0.15$ and 0.08 mms⁻¹) and singlet with $\delta = -0.04$ and -0.06 mms⁻¹ respectively. The doublet in the Mössbauer spectrum is due to formation of Fe(III) in low spin state. These may be due to the partial decomposition of the complex. In substituted complex, ΔE_Q value is slightly increased at 300 °C compared to those for room temperature. The weight loss shows complete removal of water molecules, this is supported by infrared spectra which decrease in intensity of the absorption band due to water molecule. The removal of coordinated water molecule changes the s-electron density at the iron nucleus. Dehydration of pentacyanoferrates(II) affect the crystal structure of the complexes without changing the cubic symmetry of the iron nucleus. The isomer shift of the potassium hexacyanoferrate(II) trihydrate increase on dehydration[21]. A similar trend has been observed in the present case.

At 500 °C, a drastic change occurred in the Mössbauer spectrum as indicated by 7 lines with a singlet (Fig.2D) and may be resolved into one set of sextets with $H_{\text{eff}} = 217$. These may correspond to the formation of Fe_3C . The Mössbauer spectrum of the 750 °C consist of magnetite, metal carbides and supermagnetic peaks (Fig.2E). In this spectrum six lines due to iron carbides were observed clearly. The spectrum at 700 °C, consist of α -Fe and magnetite with small amount of supermagnetic peaks (Fig.2F) Thus fine superparamagnetic peaks observed at 750 °C samples were confirmed to be α -Fe and magnetite. This is confirmed by 2-3 sextets with $H_{\text{eff}} = 331$ and 463 kOe respectively. In order to identify the end product of substituted complex, these have been further heated at 950 °C. At 950 °C, the Mössbauer spectrum is much resolved displays the classical 12 lines The Mössbauer spectrum exhibits well resolved sextet (Fig.2F) with $H_{\text{eff}} = 514, 501, 462\text{kOe}$.

The XRD pattern of the compound heated at different temperature; a single phase spinel is formed as all the peaks are match well with the characteristics reflection of ferrites. The peaks are broad indicating the fine crystalline nature of the ferrite formed. For the calcined samples (B to E) also all the characteristics reflections of sodium ferrites are seen with increased intensity and sharpness. It indicates progressive growth of crystalline and better crystallinity after calcined at higher temperatures. This is due to the formation of hematite and α - Fe_2O_3 as supported by XRD data[22].

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