



SYNTHESIS OF NANOSIZED FERRITE FROM THE THERMOLYSIS OF DIPHENYLAMINE SUBSTITUTED PENTACYANOFERRATE COMPLEXES

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Abstract- 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 diphenylamine substituted pentacyanoferrate (II), $\text{Na}_3[\text{Fe}(\text{CN})_5\text{L}] \cdot x\text{H}_2\text{O}$ where L= diphenylamine 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 and end products and

nanostructured materials. Mössbauer spectra of these complexes exhibits quadrupole doublet with $(\Delta E_Q) = 0.74 \text{ mms}^{-1}$ at room temperature and isomer shift $(\delta) = 0.00 \pm 0.03 \text{ mms}^{-1}$ suggests that the iron atom is in the $=+2$ low spin state. Thermogram of diphenylamine substituted complexes show multistage decomposition. The complexes start decomposing at 50°C yielding residual weight 17.9% at temperature

890 °C. The Mössbauer spectra recorded after heating at 300°C exhibit single line suggesting partial decomposition. At 400 and 500 °C, six lines pattern start appearing which on further heating at 600, 700 and 950 °C turns into three sextet suggesting the formation of mixture

$\text{Fe}_3\text{O}_4(\text{A})$, $\text{Fe}_3\text{O}_4(\text{B})$, Fe_3C and $\alpha\text{-Fe}_2\text{O}_3$. The temperature of ferrite formation is much lower than possible in the conventional ceramic method.

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Introduction

Superparamagnetic iron oxide nanocrystals have been found application in different fields, from e.g. magnetic recording media to cancer treatment by hyperthermia¹. The need of high resistivity ferrites led to the synthesis of their magnetic materials by various techniques. Since the formation of ferrites by the conventional method has several disadvantages, viz, non homogeneity, large particle size, low surface area and poor sinterability, the precursor technique have been undertaken to prepare fine particles of sodium ferrite. This method has been applied successfully for obtain of several metal ferrite from thermolysis of their respective pentacyanoferrates. Earlier we have studied several alkyl and aryl

amine substituted pentacyanoferrate(II) complexes²⁻⁴. Coelho et al⁵ 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 materials⁶. Brar and Varma⁷ studied thermal decomposition product of sodium pentacyanoferrate(II) using Mössbauer spectroscopy. Sielo et al⁸ 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 decomposi-

tion to confirm the differences in the particle size and chemical state of iron oxides. In order to characterize their Mössbauer spectroscopy, XRD and electron microscopy were used.

Experimental Preparation of substituted pentacyanoferrate(II) complexes 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}Co (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. The DSC Curve was recorded between 273K and 785K on RIGAKU Thermoflex Apparatus at scanning rate 5Kmin⁻¹. XRD of decomposition products were recorded using MAC science MXP-18 automated diffractometer by Cu-K α radiation.

A solution containing 0.47g of hydroxylamine hydrochloride and 0.54g NaOH in 20 mL water was prepared. Then 10% ligand (L= diphenylamine) 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.

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Results and Discussion

The complex was coloured solid and stable under normal atmospheric conditions. Electronic spectral bands and characteristic IR

frequencies due to $\nu(\text{C}\equiv\text{N})$, $\delta(\text{Fe-CN})$ and $\nu(\text{Fe-C})$ are listed in Table 1. ^{57}Fe Mössbauer spectra of all the complexes exhibit a well resolved quadrupole doublet at room temperature. Typical Mössbauer spectra of diphenylamine substituted pentacyanoferrate(II) complexes at room temperature and after heating at different temperatures are shown in Fig.1. 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.

Table 1- IR frequencies and Electronic spectral band for substituted pentacyanoferrate(II)

Sr. No	Complex $\text{Na}_3[\text{Fe}(\text{CN})_5\text{L}]\text{L}'$	IR Frequencies (cm ⁻¹)			Electronic spectral band /cm ⁻¹
		$\nu(\text{C}\equiv\text{N})$	$\delta(\text{Fe-CN})$	$\nu(\text{Fe-C})$	
1	(n-C ₅ H ₁₁) ₃ N	2045m	575m	430s	20000, 25000

Table 2- Mössbauer parameters for substituted pentacyanoferrate (II) and its thermal decomposition products

Complex $\text{Na}_3[\text{Fe}(\text{CN})_5\text{L}]\text{L}'$	Temp	Isomer shift, δ , mms ⁻¹	Quadrupole splitting, ΔE_Q , mms ⁻¹	Heff/ kOe	Possible products	
(n-C ₅ H ₁₁) ₃ N	25	0.00	0.074	-	-	
	300	0.22	0.74	-	-	
		-0.07	-	-	-	
	400	0.26	0.03	491	Fe ₃ O ₄ (A)	
		0.63	-0.01	459	Fe ₃ O ₄ (B)	
		-0.07	-	-	-	
	500	0.26	0.06	496	Fe ₃ O ₄ (A)	
		0.65	-0.02	463	Fe ₃ O ₄ (B)	
		-0.06	-	-	-	
	600	0.27	-0.04	490	Fe ₃ O ₄ (A)	
		0.71	-0.02	464	Fe ₃ O ₄ (B)	
		0.19	0.01	210	Fe ₃ C	
		700	0.26	-0.03	493	Fe ₃ O ₄ (A)
			0.70	-0.02	463	Fe ₃ O ₄ (B)
	800	0.00	0.00	331	□-Fe	
		0.85	0.73	--	--	
0.36		0.46	--	--		
950		0.38	0.14	521	□-Fe ₂ O ₃	
		0.37	0.03	502	Fe ₃ O ₄ (A)	
	0.54	0.02	464	Fe ₃ O ₄ (B)		

Various vibrational modes were assigned by the comparison with the other substituted pentacyanoferrate(II) complexes¹⁴⁻¹⁵. The

most intense band due to $\nu(\text{C}\equiv\text{N})$ observed in the range 2090-

2010 cm⁻¹. Earlier, three modes of $\nu(\text{C}\equiv\text{N})$ have been observed for some di and trialkylamine substituted pentacyanoferrate(II)

complexes^{3,4}. A strong to medium intensity band due to $\nu(\text{C}\equiv\text{N})$ was observed at 2045cm⁻¹. A very weak band observed at 430

$\pm 10\text{cm}^{-1}$ has been assigned to $\nu(\text{Fe-C})$ according to assignments of Fluck et al⁸.

This compound show large quadrupole splitting (ΔE_Q) indicating

quite significant distortion in octahedral geometry. Since all the six

$3d$ electrons forms a closed shell t_{2g}^6 , no quadrupole splitting is expected due to valence electron configuration. However, due to substitution of sixth cyano with ligand, distortion in octahedral geometry is expected. Therefore, (ΔE_Q) is direct measure of the distortion due to ligand contribution although small electronic contribution may also be expected due to further lifting of degeneracy

in t_{2g} level is suggested by Manoharan and Gray¹⁶ for sodium nitrosyl ferrate(II). 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 geometry¹⁹.

The simultaneous thermal analysis (TGA, DTG and DTA) thermograms of diphenylamine substituted pentacyanoferrate(II) complexes at a heating rate 15°C per min. A slope in TG at a mass loss of 13.0 and 11.0% at 395 and 406K respectively indicating the removal of the 4-5 water molecules. DTG peak corresponding to this step is centered at 548K which is endo in DTA with peak at 567K. At the end the mass loss of 17.9-21.0 % in the TGA curve for the removal of remaining water molecule (Calc. loss 18.1-22.1%).

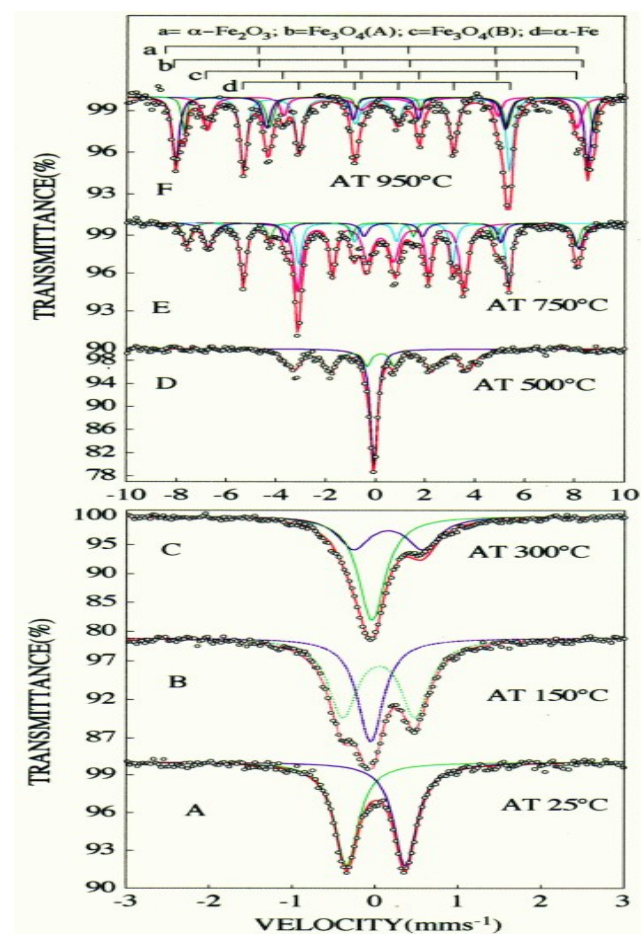


Fig. 1- Mössbauer spectra of diphenylamine submitted pentacyanoferrate(II) complex at (A) room temperature and after heating at (B) 25°C , (C) 300°C , (D) 500°C , (E) 750°C and (F) 950°C for 3 hrs.

Mössbauer spectroscopy is a good tool for examining the various iron species formed during the decomposition of an iron complex. It is possible to distinguish not only between Fe^{2+} and Fe^{3+} species, but also between their modes of coordination. The parameters used are the isomer shift, quadrupole splitting and hyperfine field. By means of these parameters, earlier researchers⁹⁻¹¹ was able to identify the different iron species in iron complexes. Ganguli and Bhattacharya¹¹ concluded that Prussian blue exhibits semiconducting behavior in the temperature range $30\text{-}150^\circ\text{C}$ with different stages of hydration. Inoue et al¹² reported on the thermal decomposition of Prussian blue and identified various products by Mössbauer spectroscopy.

Mössbauer spectra of substituted pentacyanoferrate(II) complex heated at 300°C for 3 hr exhibit an asymmetric doublet typically shown in Fig.1B which may be further resolved into quadrupole and singlet. In substituted complex, ΔE_Q value is same 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 dehydration²¹. A similar trend has been observed in the present case.

At 400 and 500°C , a drastic change occurred in the Mössbauer spectrum as indicated by 7 lines with a singlet (Fig.1C, 1D) and may be resolved into two set of sextets with $H_{\text{eff}} = 490$ and 470 kOe . These may correspond to the formation of Fe_3O_4 . The Mössbauer spectrum of the 600°C consist of magnetite, metal carbides and supermagnetic peaks (Fig.1E). In this spectrum six lines due to iron carbides were observed clearly. The spectrum at 700°C , consist of $\alpha\text{-Fe}$ and magnetite with small amount of supermagnetic peaks (Fig. 1F) Thus fine superparamagnetic peaks observed at 600 and 700°C samples were confirmed to be $\alpha\text{-Fe}$ and magnetite. This is confirmed by 2-3 sextets with $H_{\text{eff}} = 330$ and 460 kOe respectively. The doublet gives $\Delta E_Q = 0.73 \text{ mms}^{-1}$ and $\delta = 0.86 \text{ mms}^{-1}$ which may be attributed to NaFeO_2 (Fig.1F). 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.1G) with $H_{\text{eff}} = 521, 501, 464 \text{ kOe}$. This is due to the formation of haematite and $\alpha\text{-Fe}_2\text{O}_3$ as supported by XRD data²².

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