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Original Article

Synthesis of A novel aminoalkoxide of iron by oxide one-pot process: Its sol-gel application to iron oxide powder

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Abstract

A low-cost and facile route to synthesize ferratrane complex, which can be employed as alkoxide precursor for iron oxide or doped iron oxide via sol-gel technique, has been developed from the reaction of a very inexpensive and plentiful starting materials via the oxide one-pot synthesis (OOPS) process. Ferratrane complex was directly synthesized from iron hydroxide, triethanolamine and ethylene glycol in the presence of triethylenetetramine as catalyst. The structure of resulting products was fully characterized using FTIR, ^{1}H, ^{13}C-NMR, elemental analysis, mass spectroscopy and TGA. Moreover, the influence of calcination temperature on the formation of iron oxide powders prepared by sol-gel route using the synthesized ferratrane complex was investigated. The microstructure, morphology and electrical property of iron oxide obtained were also elucidated.

Keywords: ferratrane, triethanolamine ligand, sol-gel, iron oxide

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1. Introduction

Iron oxide material is one of the most important materials for a wide range of applications, e.g., magnetic recording, energy storage, photo-electrochemistry, photoelectrodes, catalysis, electrochromism, sensor and nonlinear optics materials (Sivakov *et al.*, 2005; Yuan *et al.*, 2004; Zhang *et al.*, 1997; Berger *et al.*, 2001). Iron oxide powders are prepared by a large variety of techniques which include hydrothermal synthesis, precipitation, thermal decomposition, emulsion and sol-gel techniques (Bakardjieva *et al.*, 2005; Özer *et al.*, 1998; Pich *et al.*, 2005; Diamandescu *et al.*, 1999). The sol-gel route has advantages over other techniques, such as compositional and microstructure control, wide variety in shape fabrication and low processing temperature. Additionally, the metal alkoxide precursors used in sol-gel process give homogeneity and high purity of metal oxide products although they are greatly moisture sensitive and more expensive. However, the high reactivity of metal alkoxide precursor is the major obstacle during the fabrication. The synthesis of novel metal alkoxide precursor is necessary for the development of metal alkoxide chemistry and the investigation in sol-gel field.

Generally, the atrane complexes are performed by means of trans-esterification reaction, using alkoxide derivatives in non-aqueous dried solvent under an inert atmosphere.

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The procedure is quite complicated. Furthermore, alkoxide starting materials used for the synthesis of atrane complexes are commercially expensive (Menge *et al.*, 1991; Nugent *et al.*, 1994). The oxide one-pot synthesis (OOPS) process is a cheap, simple and straightforward process for preparing highly moisture stable and pure metal alkoxide precursors using inexpensive and readily available starting materials. Ferratrane, one of the atrane complexes, is an aminoalkoxide derivative of iron metal. The main focus of the present work is in the synthesis of a novel atrane compound of iron metal by OOPS process, to be further used as a precursor for barium ferrite, nickel ferrite, strontium ferrite, etc. and the preparation of iron oxide material directly from the synthesized ferratrane via sol-gel route.

2. Experimental

2.1 Materials

UHP grade nitrogen (99.9% purity) was obtained from Masser Specialty Gas Company Limited. Ethylene glycol, triethanolamine, triethylenetetramine and acetonitrile were purchased from Carlo Erba Reagent. Anhydrous diethyl ether was acquired from Lab-Scan Company Limited. Dichloromethane was purchased from Baker Analytical Company Limited.

2.2 Preparation of ferratrane

The synthesis of 2,2’,2’’-aminotriethoxyiron (ferratrane) was carried out in one step by mixing iron hydroxide (0.10 mol), triethanolamine (TEA, 0.15 mol) and triethylenetetramine (TETA, 0.32 mol) in a simple distillation set using 20 ml of ethylene glycol (EG) as solvent. The reaction mixture was heated to the boiling point of ethylene glycol to remove any liberated water from the reaction under nitrogen atmosphere. After 2 h, the solution was virtually clear, indicating reaction completion. The mixture was cooled to room temperature, and acetonitrile, anhydrous diethyl ether and dichloromethane used as precipitants were added. The product precipitated out as a solid. The solid was filtered off, washed three times with acetonitrile and dried under vacuum at room temperature.

2.3 Sol-gel processes

Some preliminary observation of iron oxide preparation via sol-gel process was carried out by hydrolyzing ferratrane complex by water at hydrolysis ratio (h = $[H_2O]/[Fe]$) of 8. The reaction was performed at room temperature with continuous stirring. The solution mixture was aged for at least 5 h. The product was finally calcined in a furnace at various temperatures with a heating rate of 5°C min^{-1}, and maintained at the final temperature for 3 h. The heat-treated products were then characterized by SEM, XRD and electrical property.

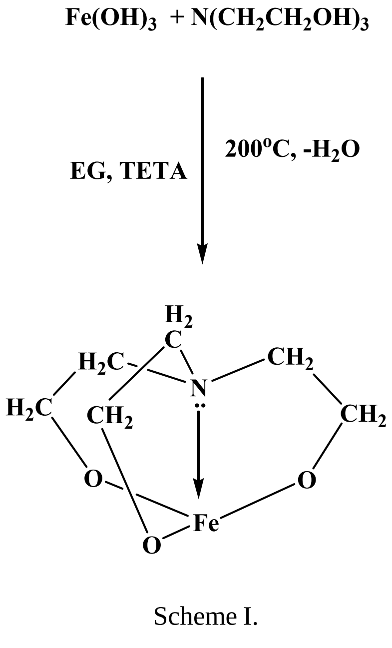
2.4 Characterization

FTIR spectra were recorded on a Bruker Optik V70.0255 spectrometer (Germany) with a spectral resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) was accomplished using a Perkin Elmer TGA7 with a heating rate of 10°C min^{-1}. NMR characterization was carried out on a Bruker AV300 spectrometer (300MHz), using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and reference for chemical shift measurement. The Maldi-TOF mass spectroscopy was carried out on a BRUKER ReflexIV. Elemental analysis (EA) was performed on a CHNS/O analyzer (Perkin Elmer, PE-2400). The structure of the phases in the iron oxide material obtained using ferratrane via sol-gel process after calcination at various temperatures was identified by a Bruker D8 Advance powder diffractometer using Cu Kα radiation (λ = 0.154 nm). Sample microstructure was investigated on a Hitachi S3400 SEM apparatus. Electrical property of iron oxide obtained from the calcination of sol-gel derived iron oxide gel was measured using four-point probe (Lucas Labs, 302Resistivity Probe). The current-voltage characteristics were measured using a Keithly 6517A digital electrometer and stabilized power supply.

3. Results and Discussion

3.1 Synthesis

The reaction of metal hydroxide and triethanolamine (or ethylene glycol) using triethylenetetramine as catalyst is a condensation reaction liberating water as a by-product (Opornsawad *et al.*, 2001; Ksapabutr *et al.*, 2004; Piboonchaisit *et al.*, 1999). Therefore, the reaction was carried out under a nitrogen atmosphere and water was removed from the system to drive the reactions forward. In this work, the



Scheme I.

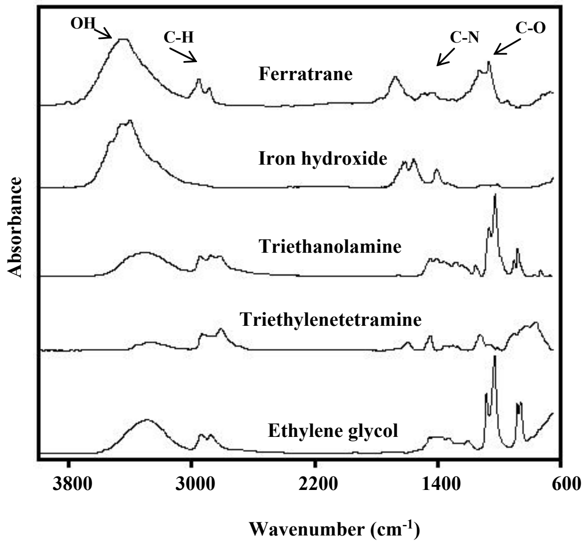


Figure 1. FTIR spectra of raw materials and ferratrane product.

reaction is demonstrated in Scheme I.

To observe the structure of ferratrane complex product, FTIR, ^{1}H- and ^{13}C-NMR spectroscopy, elemental analysis, MS and TGA were performed. The FTIR spectra of the product and its starting materials are illustrated in Figure 1. The FTIR spectrum of the synthesized ferratrane product showed the following main characteristic peaks: 3000-3681 cm^{-1} (γO-H), 2806 - 2977 cm^{-1} (γC-H), 1244 - 1275 cm^{-1} (γC-N), 1130 cm^{-1} (γC-O). In addition, a band showing at 1000-1060 cm^{-1} was attributed to C-O vibration of Fe-O-C (Glisenti *et al.*, 1998).

The ^{1}H-NMR result of the synthesized ferratrane in d$_6$-DMSO revealed peaks at chemical shifts of 2.1-2.6 and 3.0-3.6 ppm, which were assigned to N-CH$_2$ and CH$_2$-O, respectively. Similarly, the result of ^{13}C-NMR exhibited peaks at 57.1 and 59.2 ppm, corresponding to N-CH$_2$ and CH$_2$-O, respectively. Additionally, elemental analysis and mass spectroscopy were employed to confirm the structure of the synthesized product. For EA analysis, anal. Calcd. (%): C, 35.67; H, 5.99; N, 6.93 and found (%): C, 36.97; H, 6.18; N, 6.30. It was found that the obtained percentages of carbon, hydrogen and nitrogen are close to those theoretically calculated. The proposed fragmentation and structures illustrated in Table 1 obviously indicate the octamer of ferratrane (m/z 1616).

Table 1. Proposed structures and fragmentation patterns of ferratrane complex

m/z	Intensity	Proposed fragment
1616	2000	$[Fe_8C_{48}H_{96}O_{24}N_8]$-2H$^+$
1562	143	$[Fe_8C_{45}H_{90}O_{23}N_8]$-5H$^+$
1284	1566	$[Fe_7C_{36}H_{72}O_{18}N_7]$-3H$^+$
1066	3237	$[Fe_6C_{29}H_{58}O_{15}N_6]$-H$^+$
732	1449	$[Fe_5C_{17}H_{34}O_9N_5]$- H$^+$

Thermal behavior of synthesized ferratrane was studied by TGA technique. The TGA thermogram was employed to support the composition of the proposed ferratrane product. TG and DTG traces of synthesized ferratrane (Figure 2) exhibited four major weight loss peaks at about 40-130°C, 178-290°C, 295-400°C and 500-640°C which corresponded to the evaporation of precipitants and absorbed water, the decomposition of excess ethylene glycol and triethanolamine, the oxidative decomposition of the organic ligands and the oxidation of residual carbon, respectively. The percent ceramic yield for this product was 38.7% compared to 39.6% theoretical ceramic yield based on a final ceramic product of Fe_2O_3.

3.2 Sol-gel process and electrical property

Preliminary investigation of iron oxide prepared via sol-gel route showed that the structure of the resultant powders at different heat-treatment temperatures (600, 800 and 1000°C) was characterized by means of their XRD

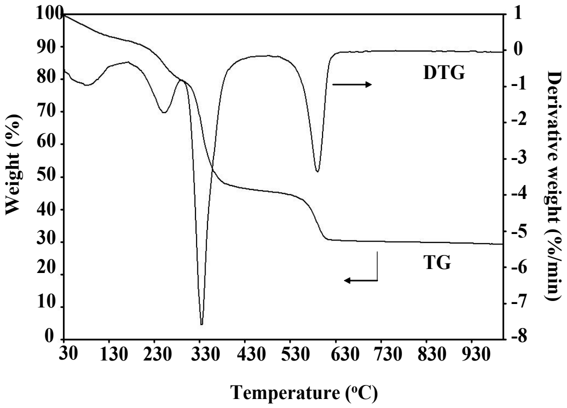


Figure 2. TG-DTG thermograms of ferratrane product.

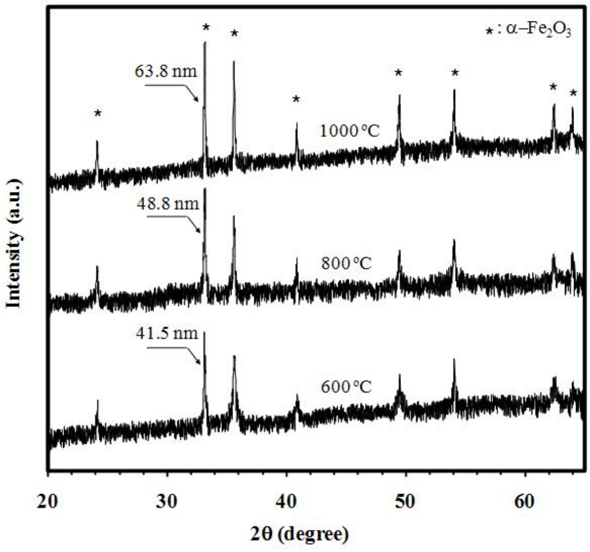


Figure 3. XRD patterns of iron oxide powders prepared at 600, 800 and 1000°C.

patterns (Figure 3), corresponding to hematite α-Fe_2O_3. It was suggested that α-Fe_2O_3 was formed since calcination at 600°C. The results of XRD also indicated that with increasing the calcination temperature the crystallinity is improved. The average size of the crystallites in the samples was calculated from Scherrer's equation (Cullity, 1978), using the most intense diffraction peaks. The α-Fe_2O_3 crystallites grew with increasing calcination temperature, from approximately 41.5 to 63.8 nm.

The SEM micrographs of the iron oxide powders are shown in Figure 4 as a function of calcination temperature. The morphology indicated a tendency of agglomeration with increasing calcination temperature, affecting the crystallite sizes, as discussed previously.

The four-point probe method of electrical resistivity measurements at room temperature shows that all iron oxide powders obtained have the resistivity values in the range of semiconductor materials (Anderman, 1998). With increasing thermal-treated temperature, the electrical resistivities tend to decrease, as demonstrated in Figure 5. This is probably due to the well-crystallized rhombohedral phase and the enhancement of crystallite size with rising the calcination temperature, leading to a decrease of both the height and width of tunneling barriers (Akl, 2004; Gross *et al.*, 2000), as revealed in XRD analysis.

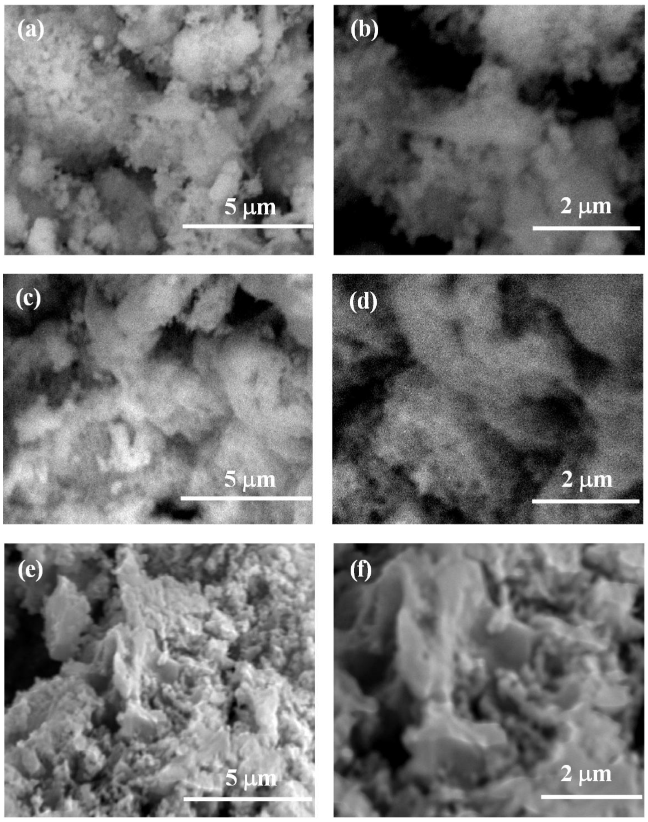


Figure 4. SEM micrographs of iron oxide powders after calcination at 600°C (magnification: 10000 (a) and 20000 (b)), 800°C (magnification: 10000 (c) and 20000 (d)) and 1000°C (magnification: 10000 (e) and 20000 (f)).

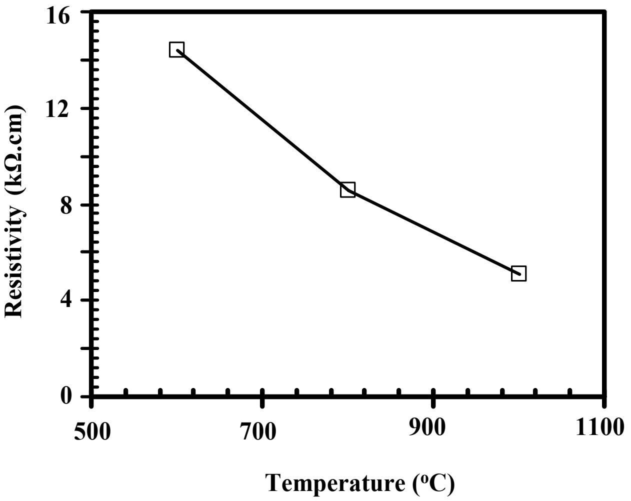


Figure 5. Electrical resistivity of iron oxide as a function of calcination temperature.

4. Conclusions

In this work, ferratrane complex, novel alkoxide precursor of iron metal with triethanolamine ligands, was successfully synthesized via the oxide one-pot synthesis (OOPS) process with a very high yield. The product has high purity as revealed by the elemental analysis data. Mass spectra result showed that product was oligomers. Additionally, the preparation of iron oxide powders using the synthesized ferratrane was also observed. The α-Fe_2O_3 nanocrystal is the main form of iron oxide produced by sol-gel process after calcination. The XRD investigation indicated rhombohedral structure. With further raising of the heat-treatment temperature, the crystallinity and crystallite size were increased. The electrical resistivity was found to be dependent on the calcination temperature. Values of the order of 10^3 and 10^4 were gained for calcination at 1000°C and 600°C, respectively.

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