Original Research article

Thermal Studies of Iron (II) Schiff Base Complexes: New Precursors for Preparation of α -Fe₂O₃ Nanoparticles *via* Solid-State Thermal Decomposition

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ABSTRACT

In this research study, four iron (II) complexes of tetradentate N₂O₂ Schiff base ligands with the general formula of Fe((MeO-bph)₂Am) (Am=1,2-ethylenediamine (1), 1,3-propanediamine (2), 1,4-buanediamine (3) and 2,2-dimethyl-1,3-propanediamine (4)) were synthesized and characterized using the elemental analysis (CHN) and FT-IR spectroscopy. Thermal properties and decomposition stages of all the complexes were evaluated. Finally, all complexes were decomposed at 600 °C for 3 h and the dark precipitates were characterized using the FT-IR, XRD and SEM. FT-IR and XRD results revealed that the precipitate were the pure phase of rhombohedral of magnetite (α -Fe₂O₃) nanoparticles. The SEM images showed that, the morphology of the precipitate was a relatively spherical shape and average diameter of 40-70 nm. The results of the thermogravimetric analysis the iron (II) complexes showed that the complexes 1-4 were stable until 140-200 °C. However, after that, all the complexes 1-4 decomposed in two stages at various temperatures.

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Graphical Abstract

Introduction

In recent years, thermal studies of the coordination chemistry of transition metal ions with Schiff base ligands is one of the best area for inorganic chemists [1-6], which is basically due to their great potential application in various fields such as antibacterial [1, 6, 7], efficient catalysts in oxidation of phenol [8, 9], elimination of Hg(II) and Cd(II) from solutions [10] and electrochemical properties [11-13]. Thermal techniques are valuable for studying the thermal behaviour of the Schiff base complexes, and for preparation of the transition metal oxide nanoparticles [3, 4, 14-16]. Hematite (α -Fe₂O₃) is the most stable iron oxide with various properties that has been widely used in various applications, prepared by different methods [17-22]. Recently, our group has reported the preparation and characterization of the NiO [14, 15], Co₃O₄ [3, 4], CuO [3, 4] and Mn₃O₄ [16], V₂O₅ [23], Mn₂O₃ [24] nanoparticles *via* solid-state thermal decomposition of Schiff base complexes. In this study, we prepared four iron (II) Schiff base complexes by template reaction of various amine, 4-methoxy-2-hydroxybenzophenone and FeCl₂·6H₂O (Scheme 1) and used them as new precursors for preparation of Fe₂O₃ nanoparticles.

Experimental

Materials and methods

All the reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analysis was carried out using a heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. Fourier transform infrared (FT-IR) spectra were recorded on a KBr disk on an FT-IR Perkin-Elmer spectrophotometer. The TG/DTA was performed using a Perkin-Elmer TG/DTA lab system 1 (technology by SII) in a nitrogen atmosphere with a heating rate of 20 °C/min in the temperature span of 50–800 °C. X-ray powder diffraction (XRD) pattern of the α -Fe₂O₃ nanoparticles was recorded using a Bruker AXS diffractometer D8 ADVANCE with Cu-K α radiation with nickel beta filter in the range $2\theta = 10^\circ$ – 80° . The morphology of the materials was assessed using a scanning electron microscopy (SEM Philips, model XL-30ESEM).

Scheme 1. Schemes of the formation of Schiff bases and their Fe(II) complex

Preparation of Fe((MeO-bph)₂bn) complex (1)

To a stirring solution of 1,2-ethylenediamine (0.1 mmol) in 5 mL CH₃OH, a solution of 4-methoxy-2-hydroxybenzophenone (0.2 mmol in 5 mL methanol) was added drop by drop. The mixture was stirred for 1.5 h to give a clear yellow solution. After that, a methanolic solution (5 mL) of MnCl₂·6H₂O was added. The final mixture was stirred at room temperature for about 10 min to give a red-brown precipitates. Red-brown precipitates were filtered, washed with cold methanol, and dried at room temperature for several days. Anal. Calcd. For C₃₀H₂₆N₂O₄Fe (1): C, 67.42; H, 4.87; N, 5.24%. Found; C, 67.53; H, 4.89; N, 5.29%. FT-IR (KBr, cm⁻¹): 3100-2800 (C-H aliphatic and aromatic), 1567 (-C=N-). 1550, 1497, 1436 (C=C aromatic).

Preparation of Fe((MeO-bph)₂pn) complex (2)

The title compound **2** was prepared according to the procedure of **1**, we used 1,3-propanediamine instead of 1,2-ethylenediamine. Anal. Calcd. For C₃₁H₂₈N₂O₄Fe (**2**): C, 67.89; H, 5.11; N, 5.11%. Found; C, 67.86; H, 5.08; N, 5.06%. FT-IR (KBr, cm⁻¹): 3100-2800 (C-H aliphatic and aromatic), 1577 (-C=N-), 1551, 1494 (C=C aromatic).

Preparation of Fe((MeO-bph)₂bn) complex (3)

The title compound **3** was prepared according to the procedure of **1**, we used 1,4-butanediamine instead of 1,2-ethylenediamine. Anal. Calcd. For C₃₂H₃₀N₂O₄Fe (**3**): C, 68.33; H, 5.40; N, 4.98%. Found; C, 68.29; H, 5.42; N, 5.01%. FT-IR (KBr, cm⁻¹): 3100-2800 (C-H aliphatic and aromatic), 1530 (-C=N-), 1479, 1430, 1415 (C=C aromatic).

Preparation of Fe((MeO-bph)₂bn) complex (4)

The title compound **4** was prepared according to the procedure of **1**, we used 2,2-dimethyl-1,3-propanediamine instead of 1,2-ethylenediamine. Anal. Calcd. For C₃₃H₃₂N₂O₄Fe (**4**): C, 68.76; H, 5.55; N, 4.86%. Found; C, 67.72; H, 5.58; N, 4.89%. FT-IR (KBr, cm⁻¹): 3100-2800 (C-H aliphatic and aromatic), 1530 (-C=N-), 1477, 1430 (C=C aromatic).

Preparation of α -Fe₂O₃ nanoparticles

For preparation of the α -Fe₂O₃ nanoparticles, 1 gr of iron (II) Schiff base complex was loaded into a crucible and then placed in the electrical furnace and heated at a rate of 10 °C/min in air, follow by a calcination at 600 °C for 3 h. Nanoparticles of the α -Fe₂O₃ were produced, washed with ethanol and dried at room temperature and characterized using the FT-IR, XRD and SEM. FT-IR (KBr, cm⁻¹): 3100-2800 (C-H aliphatic and aromatic), 1530 (-C=N-), 1477, 1430 (C=C aromatic).

Results and discussion**FT-IR spectra of complexes and α -Fe₂O₃ nanoparticles**

Figures 1-4 reveal the FT-IR spectra of the iron (II) complexes and the as-prepared α -Fe₂O₃ nanoparticles. There are several peaks in the FT-IR spectrum of each complex, such as C-H aliphatic and aromatic vibration appears at about 2900-3100 cm⁻¹. The peak correspondence to the -C=N- iminic group vibration appeared at 1567, 1577, 1530 and 1500 cm⁻¹, respectively, and finally the C=C aromatic vibration appears at about 1550-1490 cm⁻¹ for **1** and **2** and at about 1410-1480 cm⁻¹ for **3** and **4** [25, 26]. No peak was observed at about 3300-3500 cm⁻¹, confirming that there is no water molecules (coordinated and adsorbed) in the complexes. In the FT-IR spectra of the as-prepared α -Fe₂O₃ nanoparticles, there are three Fe-O vibrations at about 425, 503, and 592 cm⁻¹ for **1**, 423, 496, and

598 cm^{-1} for **2**, 424, 496, and 600 cm^{-1} for **3**, and 417, 495 and 601 cm^{-1} for **4** corresponding to $\alpha\text{-Fe}_2\text{O}_3$ [17-19, 27,28]. However, there is a broad and weak peak at 1560 cm^{-1} in the FT-IR spectra of the as-prepared $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles prepared from complexes **1** and **3**, confirmed the adsorb of water molecule on the surface of nanoparticles [27].

Figure 1. FT-IR spectra of iron (II) complex **1** and its Fe_2O_3 nanoparticles

Figure 2. FT-IR spectra of iron (II) complex **2** and its Fe_2O_3 nanoparticles

Figure 3. FT-IR spectra of iron (II) complex **3** and its Fe_2O_3 nanoparticles

Figure 4. FT-IR spectra of iron (II) complex **4** and its Fe₂O₃ nanoparticles

Thermal studies of complexes

TGA analysis is one of the most efficient techniques for the stoichiometry characteristic of various Schiff base complexes [1-3, 29]. Figure 5 demonstrates that, the thermal analysis of gravimetry (TGA) of iron (II) complexes in the N₂ atmosphere. All complexes **1–4** are stable until 140 °C, 235 °C, 200 °C and 185 °C, respectively, and confirmed that there is no solvent molecule in the complexes [30]. After that, all the complexes **1–4** decomposed in two stages at various temperatures. Thermal decomposition stages of complexes **1** and **2** are similar. The first decomposition stage for **1** is between 140–400 °C, correspondence to the elimination of 2 C₆H₅- groups (Theor. 28.8%, Exp. 28%) and the second stage is between 400–780 °C, correspondence to the elimination of 2 CH₃O-C₆H₃- groups (Theor. 39.7%, Exp. 38%).

Figure 5. TGA curves of iron (II) complexes **1–4**

For complex **2**, the first and second stages are between 235–400 and 400–780 °C, correspondence to the elimination of 2 C₆H₅- groups (Theor. 28.52%, Exp. 28%) and 2 CH₃O-C₆H₃- groups (Theor. 39.26%,

Exp. 40%), respectively. The first decomposition stage for **3** is 46% (between 200-400 °C), assigned to the elimination of 2 C₆H₅- and one CH₃O-C₆H₃- groups (Theor. 46.9%), while the second stage is 17% (between 400-780 °C), assigned to the elimination of one CH₃O-C₆H₃- groups (Theor. 19.1%).

In the first decomposition stage of **4**, 2 CH₃O- and 2 CH₃- groups (Theor. 16.2%, Exp. 17%) leave the complex. While in the second stage, 2 C₆H₅- and 2 C₆H₃- groups (Theor. 53.52%, Exp. 49%) leave the complex. Finally, at 780 °C the complexes showed that the maximum of decomposition. The stability of complexes was found to be **3**>**1** ≈ **4**>**3**.

XRD patterns of Fe₂O₃ nanoparticles

The XRD patterns of the as-prepared α -Fe₂O₃ (Figure 6) revealed the narrowest and sharpest diffraction peaks at $2\theta \approx 24.5, 33, 36, 41, 49.5, 54, 62.5$, and 64 , respectively indexed to (012), (104), (110), (113), (024), (116), (214) and (300) planes of the rhombohedral hematite phase of magnetite (α -Fe₂O₃) nanoparticles [JCPDS 89-0599] [17-22, 27-29].

Figure 6. XRD patterns of Fe₂O₃ nanoparticles prepared from iron (II) complexes **1-4**

There are no characteristic peaks of impurities and other phases in the XRD pattern, which indicates that the as-prepared α -Fe₂O₃ nanoparticles were obtained with high purity. The average particle size of the α -Fe₂O₃ nanoparticles was calculated using the Scherrer equation from full width at half maximum (FWHM) of a peak at $2\theta \approx 33$ (for predominant plane 104). According to the Scherrer equation, the average particle size was between 40-70 nm.

SEM images of Fe₂O₃ nanoparticles

The surface morphology of the as-prepared α -Fe₂O₃ nanoparticles was investigated using the scanning electron microscopy (SEM). The SEM images of the as-prepared α -Fe₂O₃ from different precursors

(Figure 7-10) revealed formation of the spherical nanoparticles. However, the average crystallite size of α -Fe₂O₃ nanoparticles prepared from complexes **1** and **2** were found to be larger than **3** and **4**, but they have shown little agglomeration compared with **3** and **4**.

Figure 7. SEM image of Fe₂O₃ nanoparticles prepared from iron (II) complex **1**

Figure 8. SEM image of Fe₂O₃ nanoparticles prepared from iron (II) complex **2**

Figure 9. SEM image of Fe₂O₃ nanoparticles prepared from iron (II) complex **3**

Figure 10. SEM image of Fe_2O_3 nanoparticles prepared from iron (II) complex **4**

Conclusions

New mononuclear iron (II) complexes of tetradentate N_2O_2 Schiff base ligands were synthesized, characterized and used as new precursors for preparation of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles. Thermal properties of complexes showed that the complexes **1-4** decomposed in two stages at various temperatures. Thermal decomposition stages of **1** and **2** are almost similar and were different by **3** and **4**. Finally, clean and pure spherical shapes of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were prepared by calcination of the complexes at 600 °C. The SEM images showed that the morphology of the as-prepared Fe_2O_3 nanoparticles was near-spherical and the average diameter of the particles was 40-70 nm. It was also observed that changing the precursor did not affect the morphology and sizes of the as-prepared Fe_2O_3 nanoparticles.

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Conflict of Interest

We have no conflicts of interest to disclose.

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