

Interlayered colored iron compounds prepared by reactions of nanoirons with bidentate chelating ligands in laponite

Dong Hwan Kim and Youhyuk Kim[†]

Department of Chemistry, College of Natural Sciences, Dankook University, Cheonan 31116, Korea

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Abstract The reaction of ammonium ferric sulfate with sodium borohydride in laponite sol yields nanoiron colloidal solution. This solution in air forms transparent yellow brown solution. The resulting solution reacts with bidentate chelating ligands. The reaction products are characterized by UV-Vis absorption spectroscopy and X-ray diffraction. All compounds show metal to ligand charge transfer band in the region of 400~650 nm in UV-Vis absorption spectra. This indicates the formation of iron-ligand complex by air oxidation of nanoiron. Also, XRD patterns exhibit that the iron-ligand complex is intercalated in the interlayer of laponite.

Key words Ammonium ferric sulfate, Laponite, Chelating ligand, UV-Vis, XRD

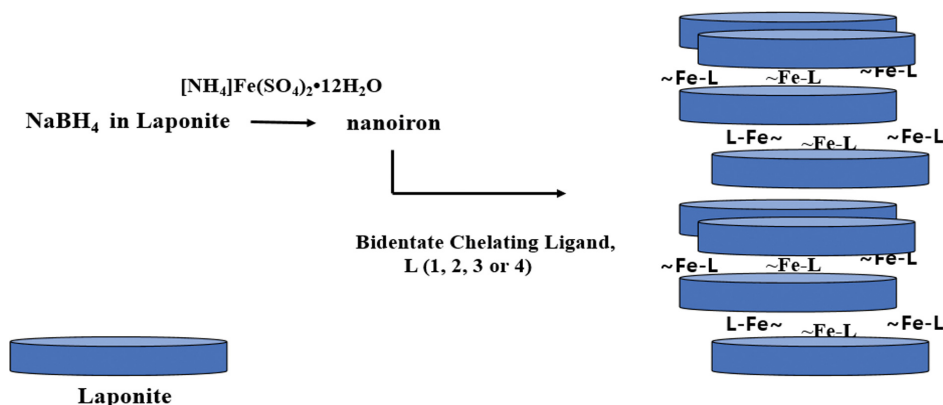
1. Introduction

There is growing interest in layered clays with inorganic particles or organic compounds between the clay layers to give novel hybrid composite systems. Inorganic or organically modified interlayered materials have a wide range of applications in chemical technologies, including chemical sensing, separations, and catalysis [1].

Laponite is a synthetic polycrystalline material similar in structure and composition to natural hectorite of the smectite group. The sodium ions in laponite are exchangeable. In aqueous dispersions, these ions in plate-like particles with negatively charged faces diffuse into the water [2-4].

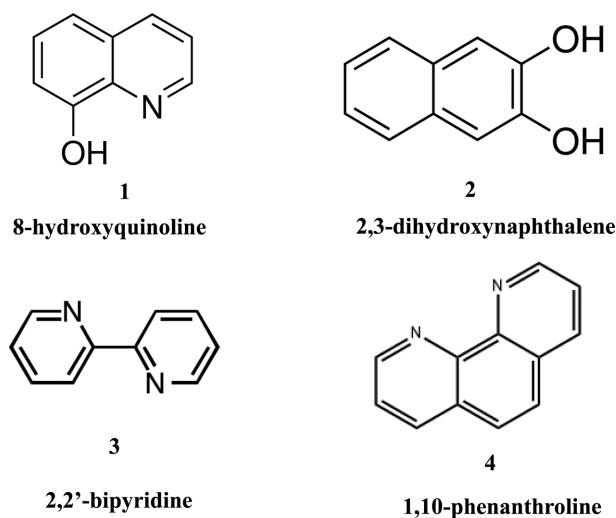
Laponite can accommodate various inorganic and organic species into its interlayer space. The preparation utilizes swelling property of laponite with water and exchangeable property of the interlayer cations with organic and inorganic guest cations [5-8]. An attempt to find new synthetic method of modified Laponite is important in order to explore numerous applications with unique thermal stability, chemical inertness due to laminar structure.

In the present study, novel synthetic method and structural characterization of iron compounds generated by the reaction of nanoirons with chelating ligands, 8-hydroxyquinoline (denoted as **1**), 2,3-dihydroxynaphthalene (denoted as **2**), 2,2'-bipyridine (denoted as **3**), and



Scheme 1. Air oxidation and reactions of nanoiron with chelating ligands, 1, 2, 3 and 4.

[†]Corresponding author
E-mail: hyukim@dankook.ac.kr



Scheme 2. Molecular structures of bidentate chelating ligands.

1,10-phenanthroline (denoted as **4**) in air are reported. (Scheme 1 and 2).

2. Experimental Section

2.1. Materials

The violet alum, ammonium ferric sulfate $[\text{NH}_4]\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and sodium borohydride NaBH_4 was used to reduce $\text{Fe}(\text{III})$. Chelating ligands, 8-hydroxyquinoline (Aldrich, 99 %), 2,2'-bipyridine (Aldrich, 99 %), 2,3-dihydroxynaphthalene (Aldrich, 98%) and 1,10-phenanthroline (Aldrich, 99 %) were used. The clay particles used in this work were laponite RDS (Rockwood Additives Ltd. U.K). Distilled water was purified using a Milli-Q Academic system (Millipore Cooperation).

2.2. Reactions of chelating ligands with nanoiron in laponite

Laponite RDS (5.0 g, 2.50 mmol of negative charge) in 500 mL distilled water was vigorously stirred for half an hour. When a laponite solution was turned to be transparent, excess NaBH_4 (Aldrich, 98 %, 0.47 g, 12.3 mmol) was added into laponite solution and stirred for 5 more minutes. Separately, analytically pure $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (0.40 g, 0.83 mmol) in 500 mL distilled water was prepared. Iron nanoparticles in laponite sol were formed by slowly dropping ammonium ferric sulfate solution into the laponite sol with NaBH_4 . The formation of iron nanoparticles was noticed by appearance of black colloidal solution. Iron nanoparticles of black col-

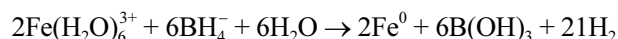
loidal solution and chelating ligands (**1**, **2**, **3** and **4**) were mixed and stirred at room temperature for 3 days. The air oxidation products were collected via freeze-dried method.

2.3. Characterization

The UV-Vis absorption spectra were recorded on a UV 2201 Shimadzu UV-Vis spectrophotometer using optical quartz cells. To understand the binding modes between iron-ligand complex and laponite in solid state, X-ray diffraction analysis was performed using X-ray diffractometer (XRD, PANalytical, X'Pert-PRO MPD, Almeldo, The Netherlands) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$).

3. Results and Discussion

The following reaction shows the reduction of ferric ions in laponite to nanoiron to yield a black colloidal solution:



When a laponite is not present in this reaction, iron particles are formed as precipitates. This iron colloidal solution became brownish yellow solution when stirring overnight in air. Since the oxidation of iron nanoparticles into iron aqua hydroxo or oxides complexes in laponite sol is complicate, this will be investigated in

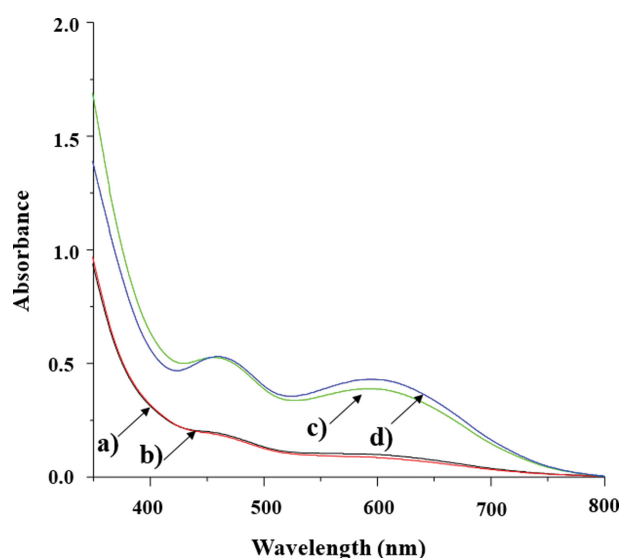


Fig. 1. UV-Vis spectra of iron-8-hydroxyquinoline complex prepared by the reaction of nanoiron with 8-hydroxyquinoline in air: nanoiron: 8-hydroxyquinoline = a) 1 : 1, b) 1 : 3, c) 1 : 6, and d) 1 : 10.

the near future [9,10].

Reactions of black colloidal sol in laponite with bidentate chelating ligands **1**, **2**, **3**, and **4** were performed. Molecular structures of ligands used in this study are shown in Scheme 2. Greenish blue and brown solutions were obtained by the reactions of black colloidal sol in laponite with bidentate chelating ligands **1** and **2**, respectively. The formation of iron-8-hydroxyquinoline complex is confirmed by the UV-Vis absorption spectra of the products. The metal-to-ligand charge transition (MLCT) band of iron-ligand adducts around 470 and

600 nm is appeared as shown in Fig. 1. The MLCT band around 470 and 600 nm of iron-ligand adducts was not observed in free 8-hydroxyquinoline.

Similarly, iron-2,3-dihydroxynaphthalene adduct shows the MLCT band around 480 nm as shown in Fig. 2. Reactions of black colloidal solution with bidentate chelating ligands **3** and **4** occur to form red solutions. The iron-ligand complex of corresponding ligand was confirmed by the UV-vis absorption spectra of the MLCT band around 470 and 540 nm as shown in Figs. 3 and 4.

To understand the binding modes between iron-ligand

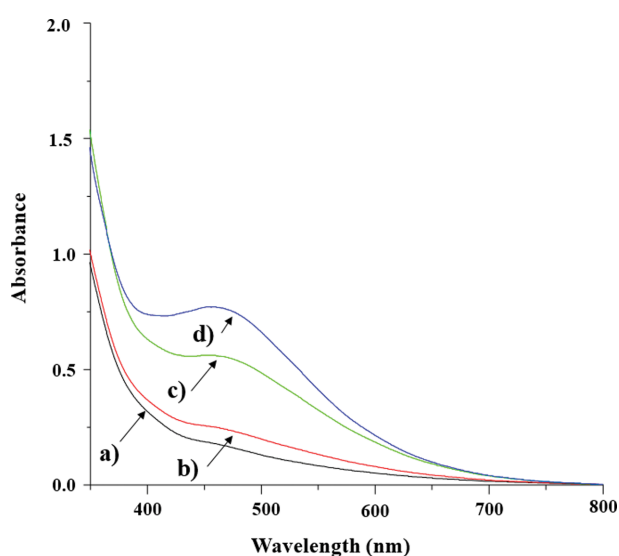


Fig. 2. UV-VIS spectra of iron-2,3-dihydroxynaphthalene complex prepared by the reaction of nanoiron with 2,3-dihydroxynaphthalene in air: nanoiron: 2,3-dihydroxynaphthalene = a) 1 : 1, b) 1 : 3, c) 1 : 6, and d) 1 : 10.

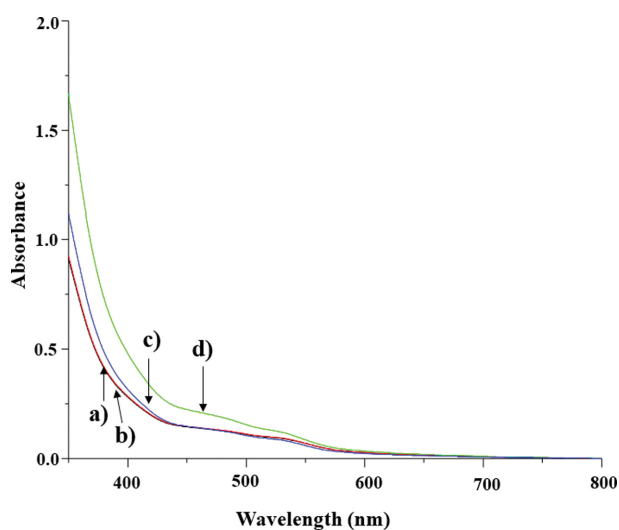


Fig. 3. UV-VIS spectra of iron-2,2'-bipyridine complex prepared by the reaction of nanoiron with 2,2'-bipyridine in air: nanoiron: 2,2'-bipyridine = a) 1 : 1, b) 1 : 3, c) 1 : 6, and d) 1 : 10.

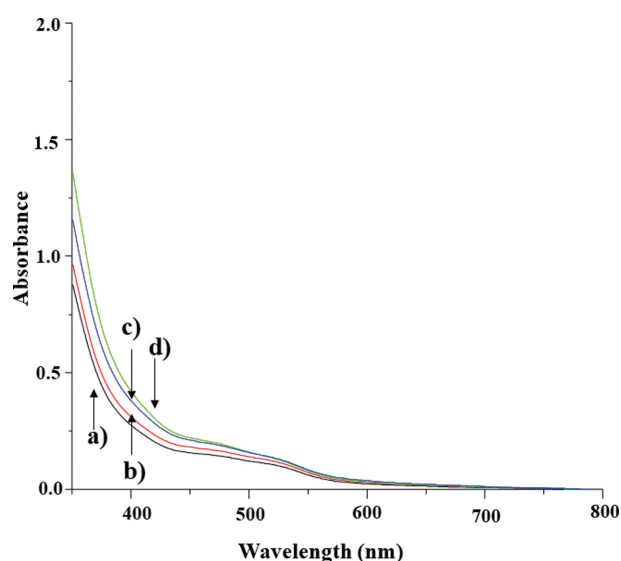


Fig. 4. UV-VIS spectra of iron-1,10-phenanthroline complex prepared by the reaction of nanoiron with 1,10-phenanthroline in air: nanoiron: 1,10-phenanthroline = a) 1 : 1, b) 1 : 3, c) 1 : 6, and d) 1 : 10.

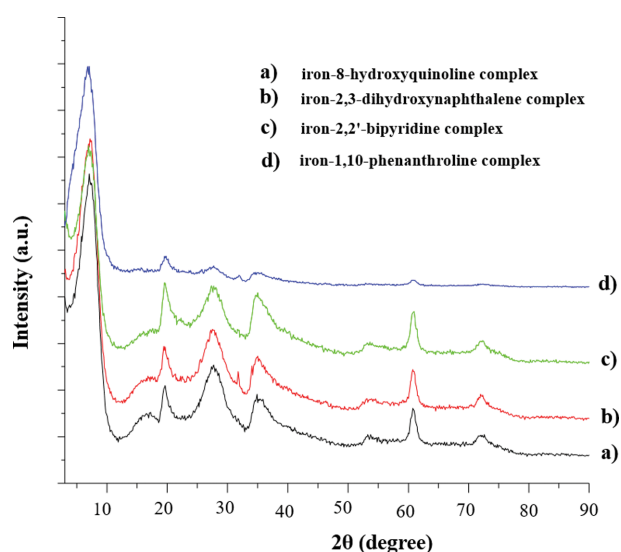


Fig. 5. X-ray diffraction patterns of iron-ligand complexes intercalated in laponite.

complex and laponite in solid state, the XRD patterns of reaction products were investigated. A sharpening of the (0 0 1) peak located around $2\theta = 8-10^\circ$ is observed as shown in Fig. 5. In general, the expansion of basal spacing of layered clay is represented by the (0 0 1) peak in the XRD patterns [11-15]. The value of the (0 0 1) plane provides the distance between the laponite layers according to Bragg's equation. The basal spacing of the Laponite-iron-ligands is in the range of 1.26~1.43 nm and is longer than that of the Laponite [16]. By subtracting the thickness of the silicate layer (0.96 nm) from the basal spacing, the height of the gallery space is estimated to be 0.30~0.47 nm [11]. This value seems to be enough to accommodate iron-ligands complexes in inclined position or straight position within the layer. These XRD results suggest that the iron-ligand complexes are intercalated within laponite without segregation. It has been reported that the $\text{Fe}(\text{bpy})_3^+$ (bpy = bipyridine) with a diameter of 1.07 nm was intercalated in inclined manner in laponite powder [15]. In this study, iron-ligands complexes are intercalated in the interlayer of laponite because having H_2O and $-\text{OH}$ ligands can produce smaller complex than solely bipyridine ligands.

4. Conclusions

The reaction of ammonium ferric sulfate with sodium borohydride in laponite sol yielded nanoiron colloidal solution, which interacts with chelating ligands to form colored solutions. These solutions exhibited a MLCT band around 470 and 600 nm in UV-Vis absorption spectra. This suggests the formation of iron-ligand complex by air oxidation of nanoiron. XRD patterns showed that the iron-ligand complex was intercalated in the interlayer of laponite.

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