



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Magnetic Nanoparticles

Magnetic nanoparticles are a class of nanoparticles which can be manipulated using a magnetic field. Such particles commonly consist of magnetic elements such as iron (Fe), nickel (Ni), cobalt (Co) and their chemical compounds. Generally, the nanoparticles are typically smaller than 100 nm in diameter (1-100 nm). The magnetic nanoparticles have been the focus of much research recently because they possess many attractive properties for using in some specific applications.

2.1.1 Iron Oxides (Cornell and Schwertmann, 2003)

Iron oxides are chemical compounds composed of iron (Fe) together with oxygen (O) and/or hydroxyl (OH). These compounds are oxides, hydroxides or oxide-hydroxides which can be called as iron oxides. Altogether, there are sixteen known iron oxides which are shown in Table 2.1. In most compounds, iron is in the Fe(III) trivalent state; but there are three compounds name FeO, Fe(OH)₂ and Fe₃O₄ containing divalent Fe(II). Iron oxides consist of close packed arrays of anions (usually in hexagonal (hcp) or cubic close packing (ccp)) in which the interstices are

Table 2.1 The sixteen iron oxides (adapted from Cornell and Schwertmann, 2003)

Oxides and hydroxides	Oxide-hydroxides
Hematite (α -Fe ₂ O ₃)	Goethite (α -FeOOH)
β -Fe ₂ O ₃	Akaganéite (β -FeOOH)
Maghemite (γ -Fe ₂ O ₃)	Lepidocrocite (γ -FeOOH)
ϵ -Fe ₂ O ₃	δ -FeOOH
Magnetite (Fe ₃ O ₄)	Feroxyhyte (δ' -FeOOH)
Wüstite (FeO)	High-pressure FeOOH
Fe(OH) ₂	Schwertmannite (Fe ₁₆ O ₁₆ (OH) _y (SO ₄) _z ·nH ₂ O)
Bernalite (Fe(OH) ₃)	Ferrihydrite (Fe ₅ HO ₈ ·4H ₂ O)

partly filled with divalent or trivalent Fe predominately in octahedral (VI) - $\text{Fe}(\text{O},\text{OH})_6$ - but in some cases in tetrahedral (IV) - FeO_4 - coordination. In some cases, small amounts of anions may also participate in the structure. There are five polymorphs of FeOOH and four of Fe_2O_3 .

2.1.2 Iron(III) Oxides (Greedon, 1994; Machala *et al.*, 2011)

Iron(III) oxides or ferric oxides are the inorganic compounds which are in the form of Fe_2O_3 . It is one of the three main oxides of iron, the other two are iron(II) oxide (FeO) which is rare, and iron(II,III) oxide (Fe_3O_4) which also occurs naturally as the mineral magnetite. As the mineral known as hematite, Fe_2O_3 is weakly ferromagnetic, reddish brown, and readily attacked by acids. There are four polymorphs of Fe_2O_3 which have the different crystal structure as shown in Figure 2.1.

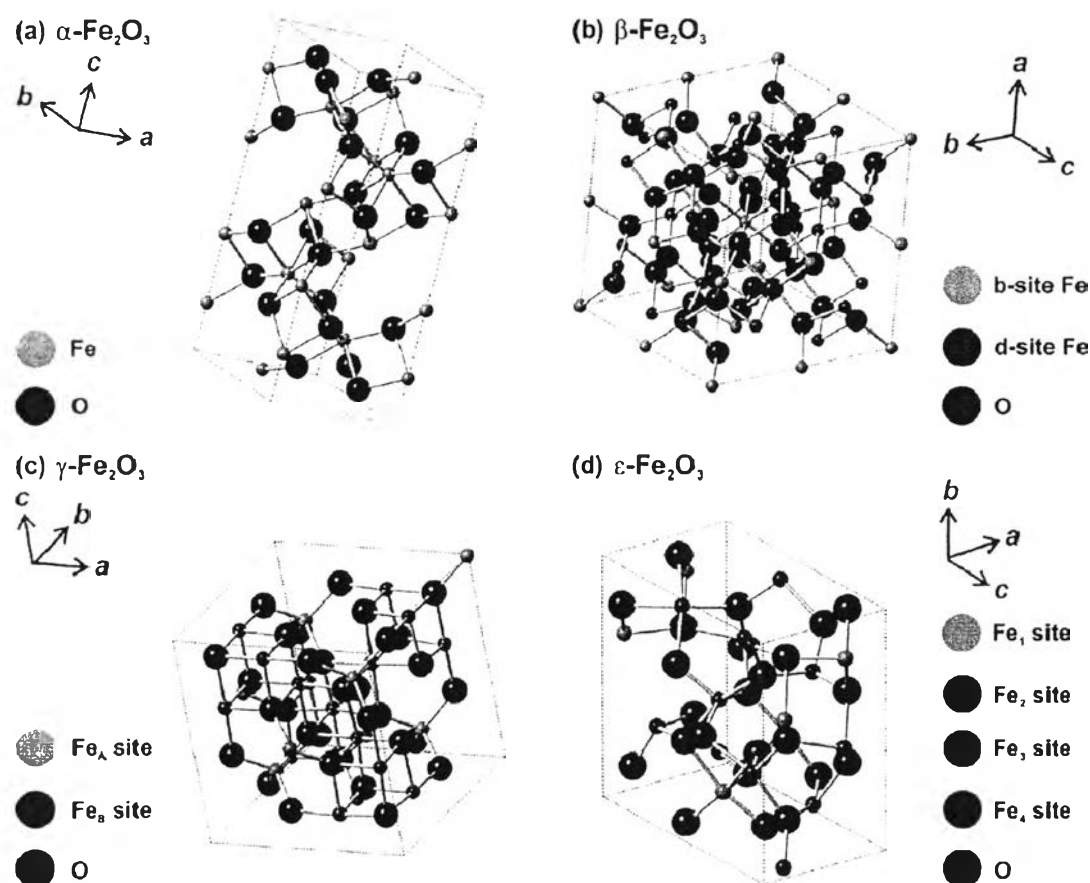


Figure 2.1 Graphical representations of the fundamental crystal structures of Fe_2O_3 : (a) $\alpha\text{-Fe}_2\text{O}_3$; (b) $\beta\text{-Fe}_2\text{O}_3$; (c) $\gamma\text{-Fe}_2\text{O}_3$; and (d) $\epsilon\text{-Fe}_2\text{O}_3$ (Machala *et al.*, 2011).

2.1.2.1 *Alpha Phase*

α -Fe₂O₃ has the rhombohedral, corundum (α -Al₂O₃) structure and is the most common form. It occurs naturally as the mineral hematite which is mined as the main ore of iron. It is antiferromagnetic below ~260 K (Morin transition temperature), and weakly ferromagnetic between 260 K and 950 K (Néel temperature). It is easy to prepare using both the thermal decomposition and the precipitation in the liquid phase.

2.1.2.2 *Beta Phase*

β -Fe₂O₃ is the cubic body centered metastable form which can be transformed into the alpha phase at temperatures above 500 °C. It can be prepared by the reduction of hematite by carbon, the pyrolysis of iron(III) chloride solution, or by the thermal decomposition of iron(III) sulfate.

2.1.2.3 *Gamma Phase*

γ -Fe₂O₃ is the cubic, metastable form which can be transformed into the alpha phase at high temperatures. It occurs naturally as the mineral maghemite which is ferrimagnetic at a room temperature and the ultrafine particles smaller than 10 nm are superparamagnetic. It can be prepared by the thermal dehydration of γ -iron(III) oxide-hydroxide, or careful oxidation of iron(II,III) oxide. The ultrafine particles can be prepared by the thermal decomposition of iron(III) oxalate.

2.1.2.4 *Epsilon Phase*

ϵ -Fe₂O₃ is the orthorhombic, metastable form which can be transformed into the alpha phase at a temperature between 500 and 750 °C. It shows properties intermediate between the alpha and the gamma phases, and has not been prepared in a pure form; it is always mixed with the alpha or the gamma phases. A material with a high proportion of the epsilon phase can be prepared by the thermal transformation of the gamma phase.

The iron oxides exist in many forms in the nature, but the most common forms are hematite (α -Fe₂O₃), magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃). These three iron oxides are also very important technologically in many applications. Some of their physical and magnetic properties are summarized in Table 2.2.

Table 2.2 Physical and magnetic properties of the iron oxides (Teja and Koh, 2009)

Properties	Hematite	Magnetite	Maghemite
Molecular formula	$\alpha\text{-Fe}_2\text{O}_3$	Fe_3O_4	$\gamma\text{-Fe}_2\text{O}_3$
Density(g/cm^3)	5.26	5.18	4.87
Melting point ($^\circ\text{C}$)	1350	1583 - 1597	-
Hardness	6.5	5.5	5
Type of magnetism	Weakly ferromagnetic or antiferromagnetic	Ferrimagnetic	Ferrimagnetic
Curie temperature (K)	956	850	820 - 986
Saturated magnetization at 300 K (Am^2/kg)	0.3	92 - 100	60 - 80
Gibbs free energy of formation (kJ/mol)	-742.7	-1012.6	-711.1
Crystallographic system	Hexagonal(rhombohedral)	Cubic	Cubic or Tetragonal
Structural type	Corundum	Inverse spinel	Defect spinel
Space group	$R\bar{3}c$ (hexagonal)	$Fd\bar{3}m$	$P4_332$ (cubic); $P4_12_12$ (tetragonal)
Lattice parameter (nm)	$a = 0.5034$, $c = 1.375$ (hexagonal); $a_{Rh} = 0.5427$, $\alpha = 55.3^\circ$ (rhombohedral)	$a = 0.8396$	$a = 0.83474$ (cubic); $a = 0.8347$, $c = 2.501$ (tetragonal)

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is the oldest known of the iron oxides and is found widespread in rocks and soils. It is also known as ferric oxide, iron sesquioxide, red ochre, specularite, specular iron ore, kidney ore, or martite. Hematite is blood-red in color if finely divided, and black or grey if coarsely crystalline. It is extremely stable at ambient conditions, and often is the end product of the transformation of other iron oxides. Magnetite (Fe_3O_4) is also known as black iron oxide, magnetic iron ore, loadstone, ferrous ferrite, or Hercules stone. It exhibits the strongest magnetism of any transition metal oxide. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) occurs in soils as a weathering product

of magnetite, or as a product of heating of other iron oxides. It is metastable with respect to hematite, and forms continuous solid solutions with magnetite.

The crystal structure of the three iron oxides can be described in terms of close-packed planes of oxygen anions with iron cations in octahedral or tetrahedral interstitial sites. In hematite, oxygen ions are in a hexagonal close-packed (hcp) arrangement, with Fe(III) ions occupying octahedral sites (Figure 2.2 (a)). In magnetite and maghemite, the oxygen ions are in a cubic close-packed (ccp) arrangement (Figure 2.2 (b)). Magnetite has an inverse spinel structure with Fe(III) ions distributed randomly between octahedral and tetrahedral sites, and Fe(II) ions in octahedral sites. Maghemite has a defect spinel structure that is similar to that of magnetite but with vacancies in the cation sublattice. Two-thirds of the sites are filled with Fe(III) ions arranged regularly, with two filled sites being followed by one vacant site.

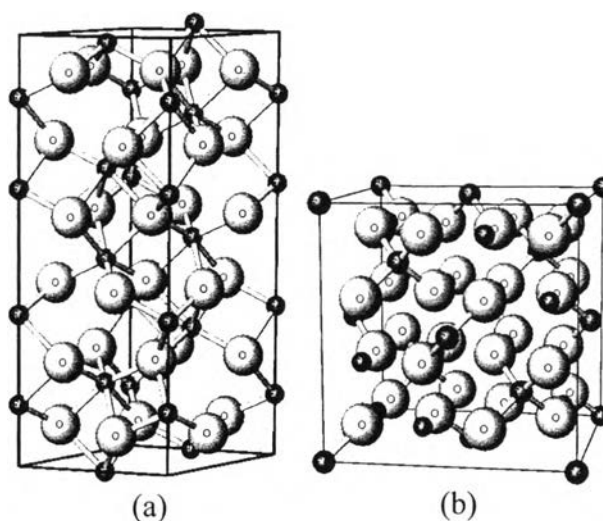


Figure 2.2 Crystal structures of: (a) hematite; and (b) magnetite & maghemite. (http://www.geocities.jp/ohba_lab_ob_page/Structure/Hematite_bond.JPG)

2.1.3 Iron Oxide Nanoparticles (Brunner *et al.*, 2006)

Iron oxide nanoparticles have attracted an extensive interest due to their superparamagnetic properties and their potential applications in many fields (although Co and Ni are highly magnetic materials, but they have limited applications due to their toxicity and susceptibility to oxidation). There are three main forms of iron oxide nanoparticles; hematite (α -Fe₂O₃), magnetite (Fe₃O₄) and maghemite (γ -

Fe₂O₃). Applications of iron oxide nanoparticles include multi-tera bit storage device, catalysis, sensors, and a platform for high-sensitivity biomolecular magnetic resonance imaging (MRI) for medical diagnosis and therapeutics. In addition, these applications require special surface modifications of iron oxide nanoparticles. Some of the common surfaces coating agents that are being used for this purpose are long chain fatty acids, alkyl amines and diols.

In almost all applications the preparation method of the nanomaterials plays a major role in determining the particle size, the shape, the size distribution, the surface chemistry of the particles, and consequently their magnetic properties. In addition, the preparation method determines to a great extent the degree of structural defects or impurities in the particle, as well as the distribution of such defects within the particle and therefore its magnetic behavior. Recently many attempts have been made to develop processes and techniques that would yield monodispersed colloids consisting of uniform nanoparticles both in size and shape.

2.2 Magnetic Behaviors

The term magnet is typically reserved for objects that produce their own persistent magnetic field even in the absence of an applied magnetic field. Only certain classes of materials can do this. Most materials, however, produce a magnetic field in response to an applied magnetic field; a phenomenon known as magnetism. There are several types of magnetism, and all materials exhibit at least one of them.

The overall magnetic behavior of a material can vary widely, depending on the structure of the material, particularly on its electron configuration. Several forms of magnetic behavior have been observed in different materials.

2.2.1 Types of Magnetisms (Spaldin, 2003)

All magnetic materials contain magnetic moments, which behave in a way similar to microscopic bar magnets. In order to define ferromagnetism as a class of magnetism, it is easiest to compare the various properties of different possible types of magnetic material. These are principally paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism as the following:

2.2.1.1 Paramagnetism

In a paramagnet, the magnetic moments tend to be randomly orientated due to thermal fluctuations when there is no magnetic field. Under an applied magnetic field, these moments start to align parallel to the field such that the magnetization of the material is proportional to the applied field.

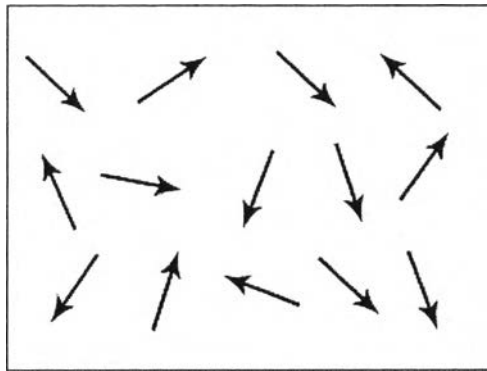


Figure 2.3 Magnetic dipole moments of paramagnetic materials (Spaldin, 2003).

2.2.1.2 Ferromagnetism

The magnetic moments in a ferromagnet have the tendency to become aligned parallel to each other under the influence of an applied magnetic field. However, unlike the moments in a paramagnet, these moments will then remain parallel when a magnetic field is not applied.

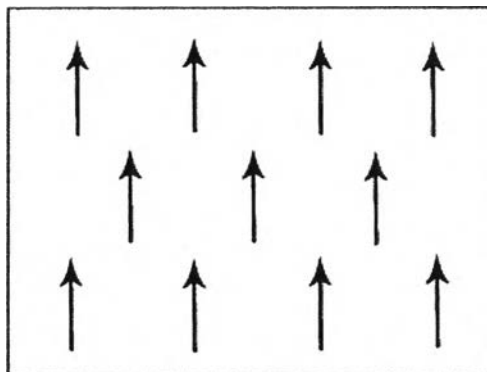


Figure 2.4 Magnetic dipole moments of ferromagnetic materials (Spaldin, 2003).

2.2.1.3 Antiferromagnetism

Adjacent magnetic moments from the magnetic ions tend to align anti-parallel to each other without an applied field. In the simplest case, adjacent magnetic moments are equal in magnitude and opposite therefore there is no overall magnetization.

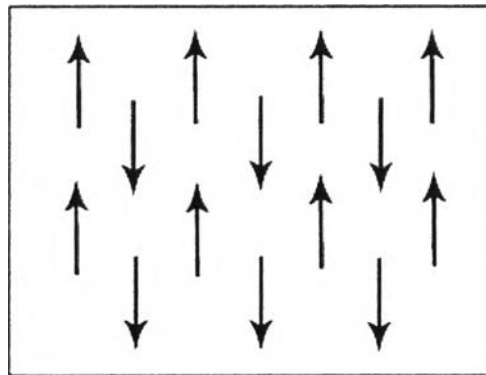


Figure 2.5 Magnetic dipole moments of antiferromagnetic materials (Spaldin, 2003).

2.2.1.4 Ferrimagnetism

The aligned magnetic moments are not of the same size; that is to say there is more than one type of magnetic ions. An overall magnetization is produced but not all the magnetic moments may give a positive contribution to the overall magnetization.

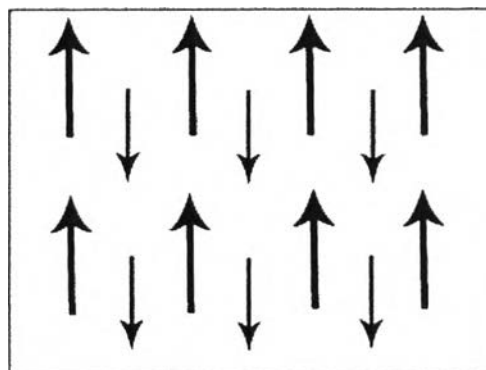


Figure 2.6 Magnetic dipole moments of ferrimagnetic materials (Spaldin, 2003).

2.2.2 Hysteresis Curve of Ferromagnetic Materials (Larson, 2006)

All ferromagnetic materials have their own atomic magnetic moments that are aligned parallel to each other within small regions called domains. In these domains, the spontaneous magnetization is equal to the saturation magnetization of the material, and the individual domains are fully magnetized all the times. In the absence of an applied field, there is no net magnetic moment or field generated by the material because the magnetization direction of each domain is randomly oriented.

During magnetization of the material, domains whose magnetization directions have a component in the direction of the applied field will grow at the expense of those that do not. Once all of the unfavorably oriented domains have been eliminated by the domain wall movement, the magnetization direction of the single domain that remains will be rotated to be parallel to that of the applied field as shown below in Figure 2.7.

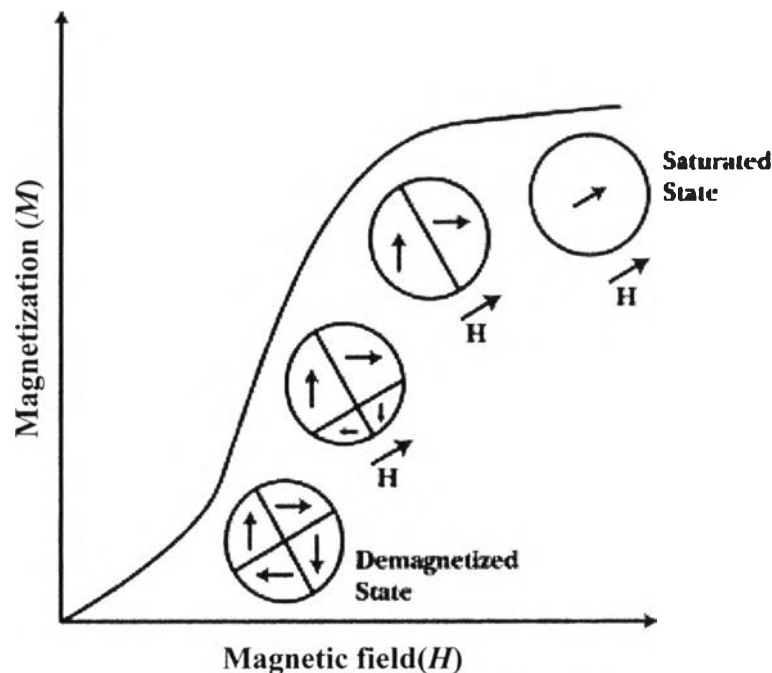


Figure 2.7 Development of magnetism in magnetic materials.

(<http://allegromicro.com/en/Design-Center/Technical-Documents/Hall-Effect-Sensor-IC-Publications/Permanent-Magnet-Publications-Dexter-Magnetic-Technologies/The-Science-of-Magnets.aspx>)

A great deal of information can be learned about the magnetic properties of a material by studying its hysteresis loop. A hysteresis loop shows the relationship between the magnetization (M) and the applied magnetic field (H). It is often referred to as the M - H loop. An example hysteresis loop is shown in Figure 2.8.

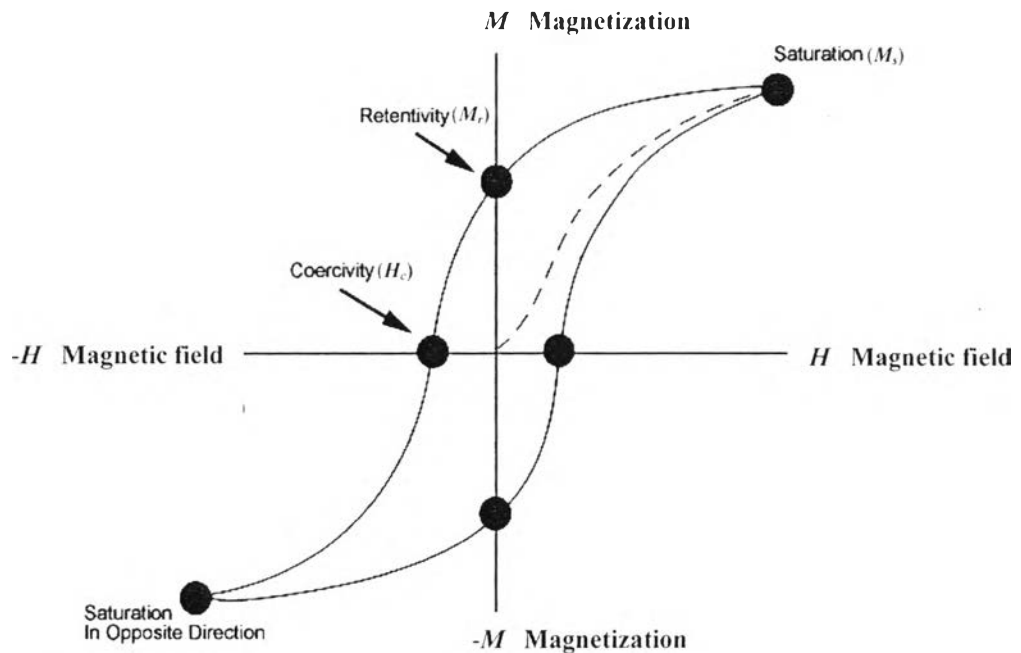


Figure 2.8 Hysteresis curve of ferromagnetic materials (Larson, 2006).

The loop is generated by measuring the magnetization (M) of a ferromagnetic material while the magnetic field (H) is changed. A ferromagnetic material that has never been previously magnetized or has been thoroughly demagnetized will follow the dashed line as H is increased. As the line demonstrates, the greater the amount of magnetic field applied (H^+), the stronger the magnetization occurred (M^+). At point "a" almost all of the magnetic domains are aligned and an additional increase in the magnetic field will produce very little increase in magnetization. The material has reached the point of saturation magnetization (M_s). When H is reduced to zero, the curve will move from point "a" to point "b." At this point, it can be seen that some magnetism remains in the material even though the magnetic field is zero. This is referred to as the point of retentivity on the graph and indicates the remanence magnetization (M_r) or level of residual magnetism in the material. As the magnetic

field is reversed, the curve moves to point "c", where the magnetization has been reduced to zero. This is called the point of coercivity on the curve. The force required to remove the residual magnetism from the material is called the coercive force (H_c) or coercivity of the material.

As the magnetic field is increased in the negative direction, the material will again become magnetically saturated but in the opposite direction (point "d"). Reducing H to zero brings the curve to point "e." It will have a level of residual magnetism equal to that achieved in the other direction. Increasing H back in the positive direction will return M to zero. Notice that the curve does not return to the origin of the graph because some force is required to remove the residual magnetism. The curve will take a different path from point "f" back to the saturation point to complete the loop.

Hysteresis curve is an important characteristic of the magnetic materials for defining their magnetic hardness. In addition, a hysteresis curve is used to measure the energy dissipated by the material during one cycle. The hard magnetic materials (Figure 2.9 (a)) have a broad hysteresis loop, a high magnetic induction, and a high coercive force in which materials are difficult to magnetize and demagnetize. On the other hand, the soft magnetic materials (Figure 2.9 (b)) have a narrow hysteresis loop, a high magnetic induction, and a low coercive force in which materials are easy to magnetize and demagnetize (Mercier *et al.*, 2002).

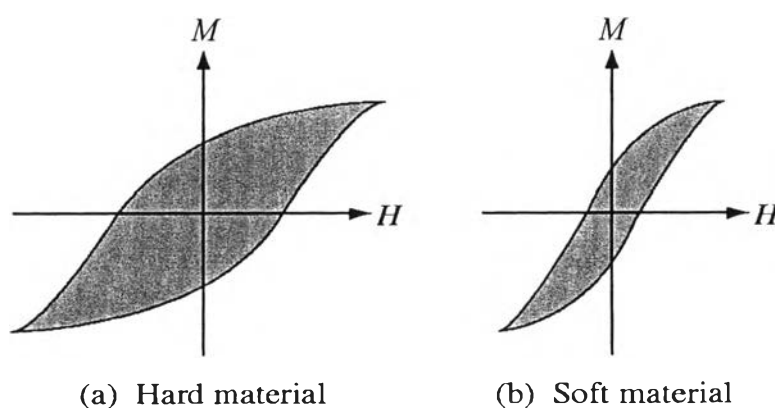


Figure 2.9 Hysteresis curves of: (a) hard; and (b) soft magnetic materials (Kacprzak, 2001).

2.2.3 Superparamagnetic Behavior (Vatta *et al.*, 2006)

The magnetic materials are subdivided into areas known as domains. In an unmagnetized sample, the moments of these domains are randomly orientated, but tend to align themselves in the direction of an external applied magnetic field. As the particle size approaches a certain minimum critical size, often in the nanoscale range, the formation of domain walls becomes energetically unfavorable. Changes in magnetization occur through the rotation of spins rather than through the motion of domain walls. Particles exhibiting these properties are called single domain. As particle size is decreased further, spins are affected by thermal fluctuations and the particles become superparamagnetic.

Magnetization behavior of ferromagnetic and superparamagnetic NPs under an external magnetic field is shown in Figure 2.10 (a), under an external magnetic field, domains of a ferromagnetic NP align with the applied field. The magnetic moment of single-domain superparamagnetic NPs also aligns with the applied field. In the absence of an external field, ferromagnetic NPs will maintain a net magnetization, whereas superparamagnetic NPs will exhibit no net magnetization due to rapid reversal of magnetic moment. Figure 2.10 (b) shows the schematic representation of the relationship between NP size and the magnetic domain structures, where D_s and D_c are the superparamagnetism and critical size thresholds, respectively (Dave and Gao, 2009).

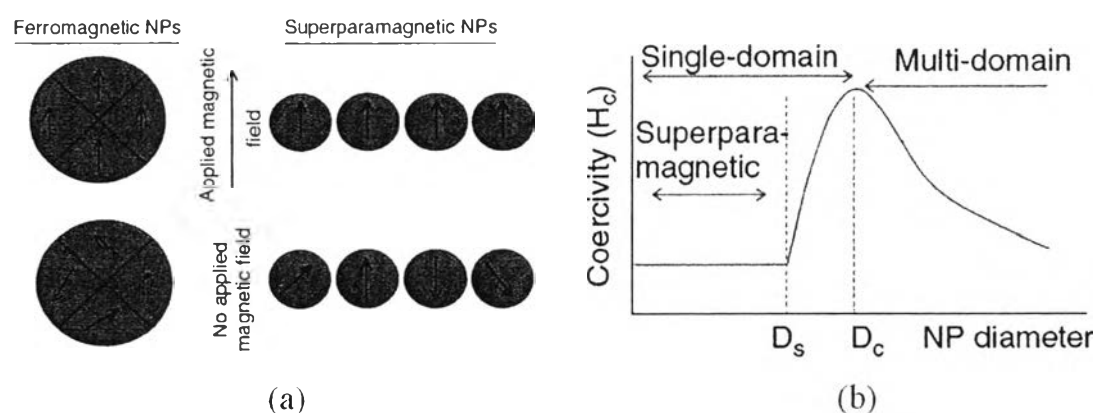


Figure 2.10 Schematic representation of: (a) magnetization behavior of ferromagnetic and superparamagnetic NPs; and (b) relationship between NP size and the magnetic domain structures (Dave and Gao, 2009).

This superparamagnetic property of materials is useful in that individual particles become magnetized only when exposed to an external magnetic field, but exhibit no remanent magnetization when the field is removed as shown in Figure 2.11. In general, the iron oxide particles which have a diameter smaller than 20 nm, usually exhibit the superparamagnetism at room temperature.

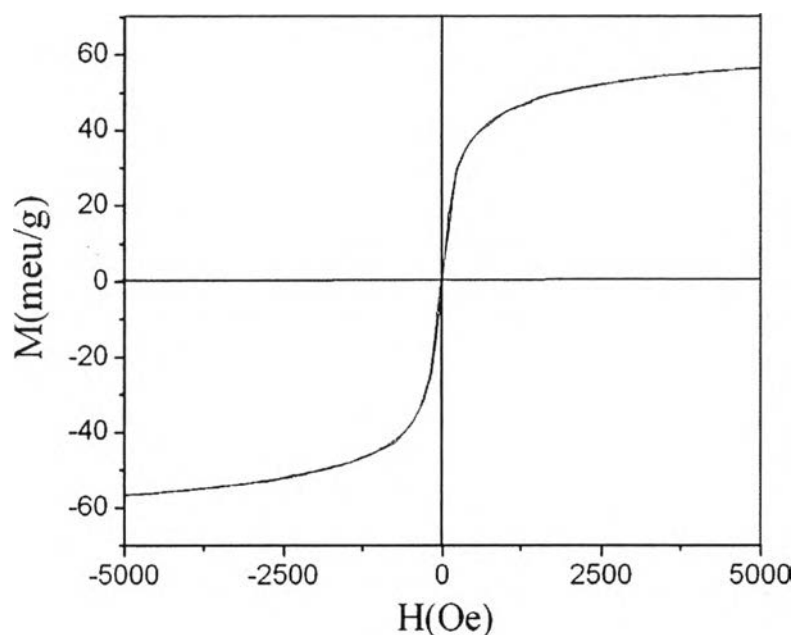


Figure 2.11 Magnetization curve of superparamagnetic materials (Wang and Jiang, 2009).

2.3 Applications of Magnetic Nanoparticles (Teja and Koh, 2009)

The magnetic properties of iron oxides have been exploited in a broad range of applications including magnetic seals and inks, magnetic recording media, catalysts, and ferrofluids, and as contrast agents for magnetic resonance imaging and therapeutic agents for the cancer treatment. These applications demand nanomaterials of specific sizes, shapes, surface characteristics, and magnetic properties.

In data storage applications, the particles must have a stable, switchable magnetic state that is not be affected by temperature fluctuations. For optimum performance in recording, the particles should exhibit both high coercivity and high re-

manence, and they should be uniformly small, and resistant to corrosion, friction, and temperature changes.

The use of ferrofluids is originally proposed for high-performance seals in space applications. Ferrofluids contain nanometer sized superparamagnetic particles disperse in aqueous or organic media. A ferrofluid has no net magnetic moment except when it is under the influence of an applied field. An external magnet is therefore able to trap the fluid in a specific location to act as a seal. They are currently employed in sealing computer disk units, and in vibrating environments in place of conventional seals. Ferrofluids exhibit a high degree of colloidal stability in a magnetic field gradient. One of the keys to improving their performance in these applications is to make the particles smaller and more uniform.

The use of magnetic nanoparticles has received considerable attention in the development of immunoassays, and targeted drug delivery vehicles, as well as in magnetic hyperthermia. These applications require particles that exhibit superparamagnetic behavior at room temperature. Remnant magnetization could lead to agglomeration of these particles, and this must obviously be avoided within the body to prevent blockage of blood vessels. In addition, applications in biology and medical diagnosis require stable magnetic particles in water at neutral pH and physiological conditions. The colloidal stability of magnetic fluids depends on the dimensions of the particles, which should be sufficiently small to minimize precipitation due to gravitation forces, and on the charge and surface chemistry. The surfaces of nanoparticles used in drug delivery are generally functionalized with drugs, proteins, and genetic materials to achieve localized delivery of these therapeutic agents.

Magnetic nanoparticles have been used *in vivo* as magnetic resonance imaging (MRI) contrast agents for molecular and cell imaging. Superparamagnetic materials are used as the core in these agents which are used to differentiate between healthy and diseased tissue. The superparamagnetic particles are generally coated with a polysaccharidic layer for colloidal stability. Magnetic particles with a polymer coating have been used in the cell separation, the protein purification, the environment and food analyses, the organic and biochemical syntheses, the industrial water treatment and biosciences. Encapsulation of magnetic nanoparticles with organic polymers is used to enhance their chemical stability, dispersability and functionality.

Another application of magnetic nanoparticles is the hyperthermia in the cancer therapy. When the superparamagnetic nanoparticles are exposed to an alternating magnetic field, they can be used to heat tumor cells to 41-45 °C, where tissue damage for normal tissue is reversible while the tumor cells are irreversibly damaged.

Magnetite and hematite have been used as catalysts for a number of industrially important reactions, including the synthesis of NH_3 (the Haber process), the high temperature water gas shift reaction, and the desulfurization of natural gas. Other reactions include the dehydrogenation of ethyl benzene to styrene, the Fischer-Tropsch synthesis for hydrocarbons, the oxidation of alcohols, and the large scale manufacture of butadiene.

Magnetite and hematite are semiconductors and can catalyze oxidation-reduction reactions. Hematite has also been used as a support material for gold in catalysts for the oxidation of carbon monoxide at low temperature. Iron oxides can be used as acid/base catalysts and to catalyze the degradation of acrylonitrile-butadiene-styrene copolymer into fuel oil. In addition, hematite has been used as a photocatalyst for the degradation of chlorophenol and azo dyes, whereas maghemite and magnetite/carbon composites have been found useful for reducing the amount of undesirable N_2 in fuel oil.

All three forms of magnetic iron oxide (hematite, magnetite, and maghemite) are commonly used in synthetic pigments in paints, ceramics, and porcelain. They possess a number of desirable attributes for these applications because they display a range of colors with pure hues and high tinting strength. They are also extremely stable and highly resistant to acids and alkalis. Pigments based on hematite are red, those based on maghemite are brown, and magnetite-based pigments are black. The transparent yellow pigments based on goethite can be transformed into the transparent red pigments of hematite by calcinations at 400-500 °C. These pigments are widely used in water-repellent stains for wood as they enable the wood grain to be seen while still providing protection against the damaging effects of sunlight. Pigments made from magnetite are also used in magnetic ink character recognition devices, and superparamagnetic magnetite particles are used in metallography for detecting flaws in engines.

2.4 Literature Review

2.4.1 Synthesis of Hematite Nanoparticles

The preparation method plays a key role in determining the particle size and shape, the size distribution, the surface chemistry and therefore the applications of the magnetic nanoparticles. In addition, the preparation method also determines the degree of structural defects or impurities present in the particles, and the distribution of such defects (Teja and Koh, 2009). Many synthesis routes have been developed to achieve the proper controls of particle size, polydispersity, shape, crystallinity, and the magnetic properties. Some of the synthesis methods have been reviewed as the following:

2.4.1.1 *Hydrolysis Method*

Raming *et al.* (2002) synthesized and studied the magnetic properties of nanosized hematite (α -Fe₂O₃) particles which were prepared through the hydrolysis reaction. The subrounded, uniform, and well-ordered crystalline hematite particles were made with an average diameter of 41 nm and a narrow particle size distribution within one day. It was found that the hydrolysis of ferric salt solutions was very sensitive to small changes in the reaction conditions, which were resulted in large variations of average hematite particle size and shape. The magnetization study revealed that magnetic behavior of the produced hematite particles changed from canted antiferromagnetic, as normal for hematite, to superparamagnetic when the particle size decreased from 160 to 41 nm.

2.4.1.2 *Hydrothermal Treatment*

Lian *et al.* (2004) synthesized the porous hematite (α -Fe₂O₃) nanorods through the hydrolysis of FeCl₃ and FeSO₄ solutions containing urea, followed with an aging under reflux conditions. In the hydrothermal condition, the porous hematite nanorods were prepared by calcination of the precursor which was obtained from hydrolysis of FeCl₃ and FeSO₄ solutions containing urea at a temperature of 90 °C for 10 h in a hydrothermal condition. It was found that the formation of the porosity of hematite was due to the decomposition of FeCO₃ and FeOOH. In addition, the results showed that the urea played a key role in the formation of the iron oxide

nanorods, and morphology of hematite particles was homogeneous in the shape of rods which were full of porosity.

Zhang *et al.* (2008) controllably synthesized and studied the magnetic properties of pure hematite (α -Fe₂O₃) nanocrystals which were prepared from a molecular precursor (ferric acetylacetonate: Fe-(ACAC)₃). Rodlike and cubiform hematite nanocrystals free of organic contaminants were controllably synthesized via the hydrothermal processing of an air-stable metallorganic molecular precursor in distilled water, simply by adjusting the low reaction temperatures (140-180 °C) and reaction times (1.5-12 h). The magnetization measurements revealed that all of the as-prepared hematite nanocrystals showed a typical superparamagnetic behavior at room temperature, except some variations in the values of remanences and coercive forces with different product morphologies.

Sun *et al.* (2010) synthesized the hematite (α -Fe₂O₃) nanoplatelets through a controlled template-free hydrothermal process. Ferromagnetic hematite nanoplatelets with diameters of 100-140 nm and heights of 40-70 nm have been successfully prepared. The homogenous products with the shape of platelet were obtained by controlling of the reaction temperature and the molar ratios of hydrosulfite ions (HSO₃⁻) to sulfate ions (SO₄²⁻). The results showed that by adjusting the molar ratio of the two kinds of ions, the obtained particles were with the shapes of short nanocolumns, polyhedral, and a mixture of nanospheres and nanoellipsoids. Room temperature magnetic hysteresis loops indicated that the prepared nanoplatelets were ferromagnetic, and had a saturation magnetization and coercivity lower than that of the short nanocolumns.

2.4.1.3 Solvothermal Process

Lu *et al.* (2006) studied the fabrication, the characterization, and the formation mechanism of a hollow spindle-like hematite (α -Fe₂O₃) via a solvothermal process. As a novel nanostructure, hollow spindle-like hematite with uniform size and morphology was polycrystalline particles with the length of 220-300 nm, the width of 70-100 nm, and the wall thickness of ca. 18 nm. It was found that these hollow-structured particles were transformed from their original solid spindle particles. During the hollow structure formation process, the interiors of solid particles were preferentially dissolved while the retained exteriors were protected by

coordinated sulfate ions. In addition, the formation mechanism was proposed as a coordination-assisted dissolution/recrystallization process which occurred in a reverse microemulsion system.

2.4.1.4 Facile Solution Route

Min *et al.* (2007) synthesized and studied the magnetic properties of hematite (α -Fe₂O₃) nanorhombohedras which were prepared through a facile solution route. The hematite nanorhombohedras with average particle size of 35 nm were synthesized through a relatively low temperature solution route. As a steric stabilizer and capping agent, PVP played an important role in the formation of the nanoparticles in the whole process. It was found that the magnetic properties of the nanorhombohedras at low temperature exhibited weakly ferromagnetic characteristic, which deviated from the behavior of the corresponding bulk material and might be ascribed to the presence of small crystals in a few regions of the sample.

2.4.1.5 Microemulsion Method

Bumajdad *et al.* (2007) studied the phase behavior and the structure of novel water-in-oil (w/o) mixed surfactant microemulsion systems which were used for the synthesis of metal oxide nanoparticles (e.g., hematite). The aqueous nanodroplets contained either a precursor reactive salt or a precipitating agent, so that a simple mixing induced nanoparticle formation. The results showed that the system was only weakly sensitive towards mono-, di- and trivalent metal salts and high ammonia levels were required for nanoparticle formation. The formation was demonstrated via the precipitation of metal oxides inside the water nanodroplets, affording the control over the resulting particle size. Moreover, the single-phase microemulsion regions of the new systems were available at around a room temperature.

Han *et al.* (2011) synthesized the hematite (α -Fe₂O₃) nanoparticles through a low-temperature microemulsion method. Nanosized hematite particles were directly synthesized by using ferrihydrite as a precursor and a trace of Fe(II) as a catalyst, by a simple microemulsion method without any requirement of a calcination step at a high temperature (e.g., 400 °C). The size of hematite particles could be controlled by regulating ω ($\omega = n\text{H}_2\text{O}/n\text{CTAB}$) value or the weight ratio of surfactant (CTAB) to oil (n-octane). The results showed that particle size increased

with the increase of ω value, and increasing the weight ratio of surfactant to n-octane was beneficial towards preparing smaller hematite nanoparticles.

2.4.1.6 Chemical Precipitation Method

Liu *et al.* (2005) studied the formation of hematite (α -Fe₂O₃) from ferrihydrite using Fe(II) as a catalyst. The adsorption of Fe(II) and the electron transfer between Fe(II) and Fe(III) played a key role in the catalytic phase transformation process. It was found that the presence of trace Fe(II), not only the dissolution of ferrihydrite was accelerated, which led to a rapid formation of hematite through a dissolution/reprecipitation mechanism, but also the solid-state transformation from ferrihydrite to hematite was also accelerated. In the former mechanism, it was possible that Fe(II) in form of FeOH⁺ took the catalytic action, while Fe(OH)₂ was a catalyst for the phase transformation in the latter mechanism.

Liu *et al.* (2007) studied the catalytic synthesis of nanosized hematite (α -Fe₂O₃) particles in solution. The spherical nanosized hematite particles were synthesized from highly condensed ferric hydroxide gel in the presence of trace Fe(II) in solution in a short time by heating the solution to reflux temperature. The results showed that size of hematite particles were controlled by regulating experimental conditions, such as pH or initial concentration of the precursor. The transformation from Fe(OH)₃ gel to hematite was triggered by the electron transfer between adsorbed Fe(II) and interfacial Fe(III). The formation of hematite could be explained by two mechanisms that were the dissolution/reprecipitation mechanism and the solid state transformation mechanism.

In comparison of all methods, the chemical precipitation method has such advantages as relatively simple and low cost (do not need some special equipment) as well as high reactant concentration, low reaction temperature, very short reaction time, less polluting, and high homogeneity as summarized in Table 2.3.

Table 2.3 Comparison of the synthesis methods for hematite nanoparticles

Method	Reactants	Reaction temp. (°C)	Reaction time (h)	Apparatus
Hydrolysis	0.02 M Fe(III) + HCl	100	24	Oven
Hydrothermal	0.02 M Fe(III) + NaHSO ₃ & Na ₂ SO ₄	220	8	Autoclave
Solvothermal	0.6 M Fe(III) + NaOH + SDBS + Dimethylbenzene	200	4-6	Autoclave
Facile Solution	0.075 M Fe(III) + PVP	140	15	Autoclave
Microemulsion	0.5 M Fe(III) + CTAB & n-butanol & n-octane	100	4.5	Flask
Chemical Pre-precipitation	1.0 M Fe(III) + NaOH + Fe(II)	100	1	Flask

2.4.2 Nucleation and Crystal Growth

The iron oxides formed in the aqueous systems usually involves the nucleation and the crystal growth steps (Schwertmann and Cornell, 2000) as follow:

2.4.2.1 *Nucleation*

Homogeneous nucleation occurs spontaneously in bulk solution when the supersaturation exceeds a certain critical value. The essential requirement for precipitation to take place is the formation of stable, embryonic clusters of molecules or ions called nuclei which is the result of collisions of ions or molecules in the bulk solution prior to nucleation. The stability of an embryo depends on a balancing between the free energy for the creation of a new interface, the interfacial or surface energy ($\Delta G_{\text{surface}}$) and the energy released by the formation of bonds in the bulk structure (ΔG_{bulk}). The free energy of nucleation (ΔG_{N}) is the sum of these two energies. Only when the embryo exceeds a certain critical size, ΔG_{bulk} is predominant and from this point, the nucleus grows by a decrease of free energy. The critical nucleus is the smallest embryo that can actually continue to grow to a crystal.

Generally, a solid can exist in two or more phases with different solubilities (such as ferrihydrite and as goethite), the initial precipitate is often the more soluble phase, although it might be expected that the less soluble phase should form first because this phase has the higher supersaturation. However, the rate of nucleation depends on interfacial energy as well as on the degree of supersaturation, so the more soluble phase may precipitate first if the interfacial energy of the critical nucleus of this phase is lower than that of the critical nucleus of the less soluble phase. From the result of the higher solubility, the initial precipitate may subsequently transform into the less soluble phase. The unstable polymorph forms first, in other words, kinetic factors overcome thermodynamics which is referred to as the Ostwald law of phases (De Yoreo and Vekilov, 2003).

Heterogeneous nucleation occurs when the presence of a solid phase reduces ΔG_N , and thus leads to an increase in the nucleation rate. The substrate may be the particles of a foreign phase or crystals (seeds) of the phase that is crystallizing. Heterogeneous nucleation can take place at a lower level of supersaturation than is required for homogeneous nucleation. The suitability of a foreign solid acted as a substrate is mainly factor for the degree of matching between structure type and atomic distances, rather than the chemical similarity of the two solids. With a good match between the structures of the crystal and the substrate, the interfacial free energy difference between a given crystal face and the substrate is lower than that between the same crystal face and the solution, so the nucleation is occurred.

2.4.2.2 *Crystal Growth*

Although a certain degree of supersaturation is needed for crystal growth, it is much less than that required for nucleation. Crystal growth involves a number of steps including diffusion of the growth units to the crystal surface and diffusion and adsorption processes at the surface itself. The overall rate of growth is determined by the slowest of these steps. The habit of the crystal is governed by the rates of growth of the different faces. Those faces which grow slowly tend to persist, whereas fast growing faces are eliminated. Foreign species which are adsorbed on the surface of the growing crystal may alter the rates at which the different faces grow and thus cause a change in crystal habit. This is a common phenomenon in the iron oxide system.

2.4.3 Catalytic Phase Transformation Mechanisms

It is known that ferrihydrite is metastable with regarding to goethite and hematite and should spontaneously transform to these minerals. Increasing temperature or a pH close to the point of zero charge (pzc) of ferrihydrite favors hematite and disfavors goethite (Liu *et al.*, 2005). It has been confirmed that hematite forms from ferrihydrite by two mechanisms consisting of solid-state transformation and dissolution/reprecipitation mechanisms as the following:

2.4.3.1 Solid-State Transformation (S-ST) Mechanism

In the solid-state transformation mechanism (Figure 2.12), the first two steps are still the adsorption of $\text{Fe}(\text{OH})_2$ and electron transfer between Fe(II) and Fe(III). Because $\text{Fe}(\text{OH})_2$, ferrihydrite and hematite share a similar hexagonal close packed anion sublattice, those oxidized Fe(II) is probably to become directly hexagonal sublattice of Fe(III). Those hexagonal sublattice aggregate and dehydrate to form the primary particles of hematite and then to grow up to be hematite particles.

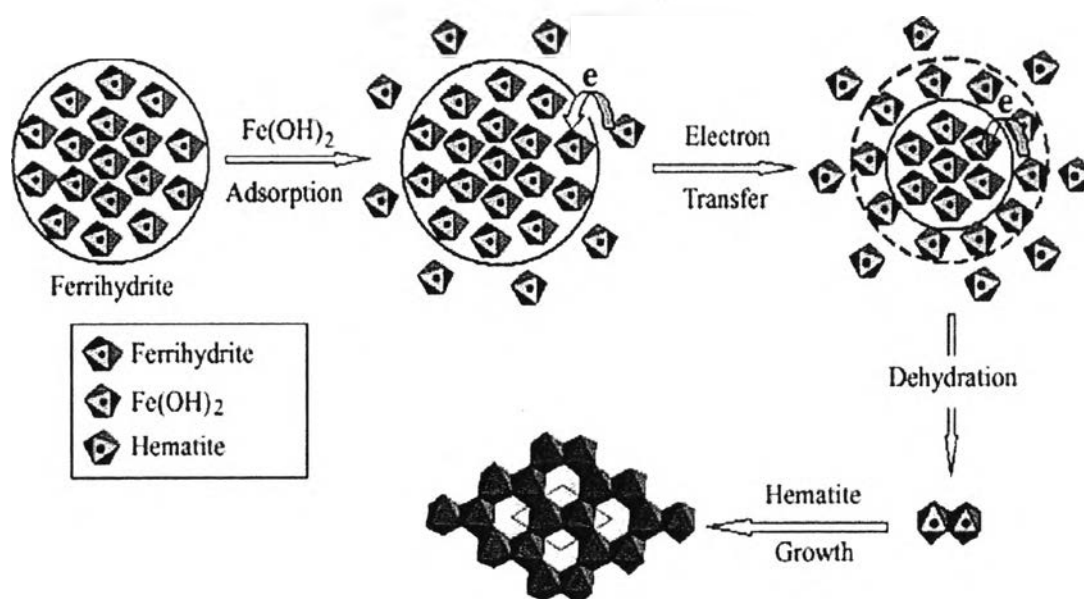


Figure 2.12 Diagrammatic sketch of the solid-state transformation mechanism of hematite (Liu *et al.*, 2005).

2.4.3.2 Dissolution/Reprecipitation (D/R) Mechanism

In the dissolution/reprecipitation mechanism (Figure 2.13), firstly, FeOH^+ is adsorbed on the surface of ferrihydrite. The electron transfer between Fe(II) and interfacial Fe(III) takes place and this electron transfer is continually repeated. Thus, the original adsorbed Fe(II) is oxidized to become Fe(III) and to detach from the surface of ferrihydrite into solution. Those Fe(III) exists in solution in form of $\text{Fe}(\text{OH})^{2+}$ or $\text{Fe}(\text{OH})_2^+$ depending on pH of the solution. Subsequently, those Fe(III) ions deposit rapidly to form hematite particles.

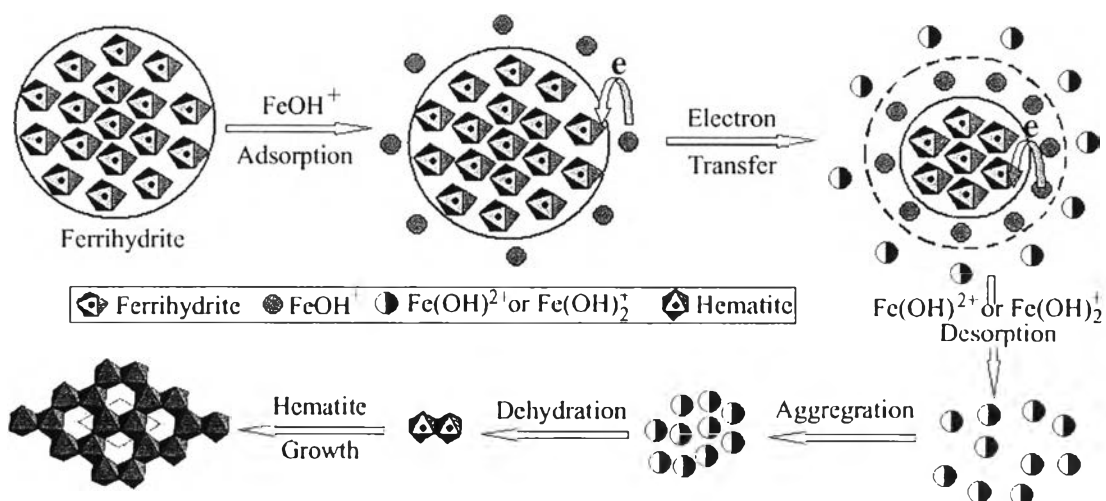


Figure 2.13 Diagrammatic sketch of the dissolution/reprecipitation mechanism of hematite (Liu *et al.*, 2005).

2.4.4 Factors Affecting the Particle Size of Hematite

According to the literature data, there are many factors affecting the particle size of the synthesized product. Some of the synthesis conditions have been reviewed as the following:

2.4.4.1 Precursor Concentration (C)

According to the literature data (Schwertmann *et al.*, 1999), the nucleation of hematite takes place within the ferrihydrite aggregate therefore the amount of Fe in the aggregate determines the final size of the hematite crystal, which is related to the aggregate size of the precursor.

2.4.4.2 Solution pH

Liu *et al.* (2005) measured the concentrations of different species of Fe(II) ions at different pHs to understand which species of Fe(II) ions played the role to accelerate the phase transformation. The Fe(II) ions existed in different forms at different pHs, as summarized in Table 2.4. They proposed that some rather than all species of Fe(II) ions played a catalytic role. Based on the literature data, the main species of Fe(II) ions involved in the catalytic action are FeOH^+ and Fe(OH)_2 . It is possible that FeOH^+ ions catalyzed the dissolution of ferrihydrite leading to the formation of hematite by a dissolution/reprecipitation process and Fe(OH)_2 accelerated the phase transformation from ferrihydrite to hematite by a solid-state reaction.

Table 2.4 Summary of Fe(II) ion forms existed at different pHs (summarized from Liu *et al.*, 2005)

Solution pH	Fe(II) ion forms	Transformation mechanism
pH 5-9	Fe^{2+} , Fe(OH)^+ , Fe(OH)_2 , Fe(OH)_3^-	S-ST and D/R
pH 5	Fe^{2+} , Fe(OH)^+	D/R
pH 7	Fe^{2+} , Fe(OH)^+ , Fe(OH)_2	S-ST and D/R
pH 9	Fe(OH)^+ , Fe(OH)_2 , Fe(OH)_3^-	S-ST and D/R

Note: The bold ion is the predominated ion in each system; S-ST and D/R stand for solid-state transformation and dissolution/reprecipitation, respectively.

2.4.4.3 Amount of Fe(II) Catalyst

Liu *et al.* (2005) determined the concentration of Fe(II) ions desorbed into the solution at different reaction time and various pHs in order to understand the action of Fe(II) ions on the phase transformation of ferrihydrite. They found that the recovery rate of Fe(II) decreased with the increasing of pH. The reasons were that some of Fe(II) ions could be absorbed on the surface of hematite particles because of their big specific surface area and Fe(II) ions might incorporate into

the product to form an impurity phase. However, the amount of Fe(II) was too small to be determined by XRD when the ratio of Fe(II) and Fe(III) was small. In their experiment, hematite particles were always the only product when $\text{Fe(II)/Fe(III)} < 0.08$ at pH 7 and $\text{Fe(II)/Fe(III)} < 0.05$ at pH 9.

2.4.4.4 Ionic Strength (I)

In the reaction process employed by Liu *et al.* (2007), Na^+ and Cl^- ions were introduced into the system via the synthetic method. They expected that Na^+ and Cl^- had little effect on the purity of the product, because it could be easily eliminated from the product by washing with distilled water. However, the presence of Na^+ and Cl^- had an effect on the size of hematite particles. The size of the particles decreased with increasing concentrations of Na^+ and Cl^- ions. This was probably because high ionic strength made the precursor flocculated and to be more aggregated.

2.4.4.5 Reaction Temperature and Reaction Time

Liu *et al.* (2010) achieved to controllably synthesize various iron (hydr)oxides from ferrihydrite by adjusting pH, temperature, time and the level of Fe(II) as well as the preparing procedure of ferrihydrite. The transformation conditions from ferrihydrite to various (hydr)oxides are summarized in Table 2.5. For the transformation from ferrihydrite to lepidocrocite, the factors such as a lower temperature (e.g. 0-25 °C), a neutral pH value and a rapid dissolution rate of ferrihydrite (e.g. the structure of ferrihydrite-2 and a high level of Fe(II)) were favorable. For the transformation from ferrihydrite to goethite, a moderate temperature (e.g. 40-60 °C) and a neutral pH value were the important factors. Both of ferrihydrite-1 and ferrihydrite-2 were transformed to hematite rapidly at pH 5-9 and 100 °C in the presence of trace Fe(II). When the transformation was completed at 60 °C, a high pH (e.g. pH 9) and a long reaction time were necessary. However, the transformation from ferrihydrite to a single product was completed under other conditions because the interconversion between iron (hydr)oxides was very complicated (Schwertmann and Cornell, 2000).

Table 2.5 Transformation conditions from ferrihydrite to various iron (hydr)oxides (adapted from Liu *et al.*, 2010)

Transformation conditions ($n_{\text{Fe(II)}}/n_{\text{Fe(III)}} = 0.02$)				Product
Precursor	pH	Temp. (°C)	Time	
Ferrihydrite-2	7	0	2 d	γ -FeOOH
Ferrihydrite-2	7	25	1 d	γ -FeOOH
Ferrihydrite-2	7	40	1d	α -FeOOH
Ferrihydrite-2	9	60	5 h	α -Fe ₂ O ₃
Ferrihydrite-2	5-9	100	0.5-2 h	α -Fe ₂ O ₃
Ferrihydrite-1	9	60	5 h	α -Fe ₂ O ₃
Ferrihydrite-1	5-9	100	15-60 min	α -Fe ₂ O ₃

Note: Ferrihydrite-1 was prepared by dropping NaOH solution into Fe(III) solution, and Ferrihydrite-2 was prepared by simultaneously adding Fe(III) and NaOH solution into a certain volume of water.