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Specific Ionic Liquids for the Synthesis of Acicular Goethite Nanoparticles

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Now-a-days preparation and study of nano particles has gain significant consideration. The common theme here is always "size matters" and over the last decades, researchers have developed exciting new materials with unique and tuneable properties. Among wide spread fields in this area, we focused on the synthesis and study of ferromagnetic iron oxides (acicular goethite) which has different application in various magnetic tapes and medical monitoring. We report synthesis of acicular goethite by using ionic liquid as a solvent and as an oxidant. With the help of [BMIM]ClO_3 the reaction time was decreased from 6 h to 2 h and oxidation reaction was took place at the lower temperature (changing from 60 ºC to 40 ºC).

Key Words: Ionic liquid, Nanoparticle, Acicular geothite.

INTRODUCTION

Room temperature ionic liquids have attracted considerable attention as solvents for different situation because they can be tuned for specific applications. Room temperature ionic liquids can be applied in industrial synthesis, separation, electrochemistry and catalysis[1-5].

Ionic liquids are organic salts, which are liquids at ambient temperatures. Unlike traditional solvents, which can be described as molecular liquids, ionic liquids are composed of ions. Their unique properties such as non volatility, non flammability and an excellent chemical and thermal stability have made them an environmentally attractive alternative to conventional organic solvents. Ionic liquids have low melting point (< 100 ºC) and remain as liquids within a broad temperature range (< 300 ºC).

One advantage of ionic liquid over the use of normal organic solvents is that the physical and chemical properties of the ionic liquids, including their polarity, hydrophobicity, viscosity and solvent miscibility, can be finely tuned by altering the cation, anion and attached substituents. This is important, because by manipulating the solvent properties, one is allowed to design an ionic liquid for specific reaction condition, such as to increase the substrate solubility or to tailor the reaction catalyst.

The first successful use of ionic liquid, dialkylimidazolium chloroaluminate, as a catalyst in Friedel-Crafts acylations[6], a number of ionic liquids with unique properties have been developed and applied to catalyze many types of reactions.

Some acidic ionic liquids, which exhibit a stable acidic anion, have been utilized to catalyze the esterification reaction and cleavages of ethers[7]. The neutral ionic liquids have also been successfully applied in the alkylation[8-11], aldol condensation[12], epoxidation[13-17] and Michael addition[18].

Recently, basic ionic liquids have aroused unprecedented interest because they showed more advantages such as catalytic efficiency and recycling of the ionic liquid than the combination of inorganic base and ionic liquid for some base-catalyzed processes[19]. A basic ionic liquid [BMIM] OH has been successfully applied to catalyze the Michael addition of active methylene compounds to conjugated ketenes, carboxylic esters and nitriles. However, the catalytic mechanism of this basic ionic liquid was ambiguous and other catalytic reactions by this basic ionic liquid are worthy for more exploration.

Recently, room temperature ionic liquids have aroused much interest as new reaction media in the inorganic nanomaterials synthetic field because there are many kinds of room temperature ionic liquids. Their solubility in water can be varied from complete miscibility to immiscibility, which can be used to prepare different morphologies of inorganic materials[18,19]. Several nanomaterials have been successfully synthesized through employing room temperature ionic liquids reaction systems, for example, TiO_2 nanocrystals[18,19], gold nanoparticles and nanosheets[20,21], palladium nanoparticles[22], nanorods and nanowires of tellurium[23], Bi_2S, Sb_2S nanorods[21] and Co-Pt nanorods. However, this new kind of reaction media still needs to be expanded in other inorganic systems.

Nano has become the new hot topic in materials science[24-35]. The common theme here is always size matters and over the last decades, researchers have developed exciting new materials with unique and tunable properties. For example, Brust *et al.*[36,37] have triggered an immense interest in gold nanoparticles, which is reflected in the dramatic increase in publications and patents with this topic.

Nanoparticles, including nano-clusters, -layers, -tubes and self-assemble systems, are seen as precursors of nanostructure materials and devices with tailored properties. Ultra fine particle engineering involves the synthesis and processing of nanometer-sized particles with controlled properties for application in advanced materials such as ceramics, metals, optical structures and semiconductors. Metals and ceramics produced by consolidating nanoparticles with controlled microstructures have been shown to exhibit properties substantially different from materials with coarse microstructures. New properties include greater hardness, higher yield strength and ductility in ceramic materials.

The aim of this work was to synthesize of acicular goethite by using ionic liquid as a solvent and as an oxidant.

EXPERIMENTAL

All chemicals were obtained as reagent grade from Aldrich and used without further purification. SEM was obtained using a LEO 1455 VP.

Synthesis of ferromagnetic iron oxides (acicular goethite): 0.07 mmol [BMIM]Br and dichloromethane (5 mL) were placed in a 3 necked round bottomed flask in an ice bath until the temperature reached 0 ºC. HNO_3 was added drop wise with the help of dropping funnel. After completing the addition of HNO_3, it was refluxed under nitrogen atmosphere. The resulting HBr was passed through water and then the reaction mixture was left under reflux for 2 h.

Product was added to 2 mL water and 0.1 mol $NaClO_3$. Mixture was stirred for 2 h and the resulting water was removed by evaporation. Then the mixture was filtered and the spectra of the solute were recorded.

In the next stage, 0.16 mol ferrous sulfate was dissolved in 37.5 mL water and 0.125 mol NaOH was added to the mixture. After 0.5 h at 40 °C, the mixture was filtered through a sintered glass funnel. The resulting precipitate was kept in furnance at 600 °C for 2 h. The magnetic characteristics of resulting particle were about 0.8 mT. SEM pictures are shown in Fig. 1.

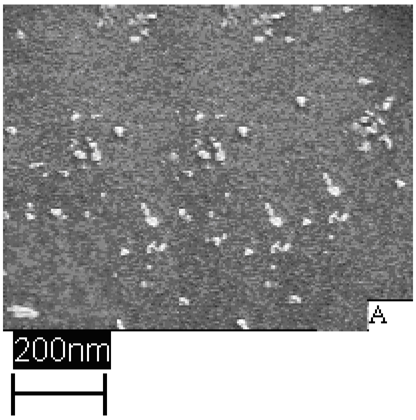

Fig. 1. A. acicular goethite produced by ionic liquid

RESULTS AND DISCUSSION

This work is related to ferromagnetic iron oxides (acicular goethite), more specifically, to a process for producing a ferromagnetic material having good stability to pressure and heat. A high coercive force which undergoes little change with time and a narrow coercive force distribution, which is capable of providing magnetic tapes with improved SP (print through) ratios and erasure characteristics. In order to satisfy such requirements, a magnetic powder having smaller particle size and higher coercive force has been required. However, it has been difficult to obtain such magnetic powder having small particle size and high coercive force by the conventional process.

It has been known to produce the acicular goethite by adding an alkali ion to an aqueous solution of ferrous salt such as ferrous sulfate, ferrous chloride, ferrous acetate, *etc.* but ferrous sulfate is preferred to give pH of higher than 11 and oxidizing it with different oxidant. The ratio between ClO_3^- and iron compound should be less than 1(0.1-0.5 are preferred).

The conventional process has the disadvantages that it takes a long reaction time for the production and the resulting acicular goethite has large particle size. On the other hand, the biggest problems in wide application of these compounds are our inability to make them in large scale and the expedition of production of these particles.

In this work, for the first time we use chlorate ionic liquid instead of potassium chlorate as both oxidant and solvent in the synthesis of acicular goethite. The resulting particle products examined by SEM and Teslameter which had the same size and the same magnetic properties as conventional methods. The reaction time was much shorter (2 h instead of 6) and at lower temperature (40 ºC instead of 60 ºC). So, for all of these reasons as well as stability and nonvolatibility of ionic liquid, we introduce $[BMIM]ClO_3$ as a better reagent for making acicular goethite than other reagent. Herein, we mentioned that preparation of $[BMIM]ClO_3$ *via* $[BMIM]NO_3$ yielded more pure compound.

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