

## Control of Crystal Phase and Agglomeration of Iron Oxide Nanoparticles in Gas Phase Synthesis

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### Abstract

*The effects of reaction temperature and precursor concentration on the microstructure and magnetic properties of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles synthesized as final products of iron acetylacetonate in chemical vapor condensation (CVC) were investigated. Pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase was obtained at temperature above 900°C and crystallite size of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles decreased with lowering precursor concentration. Also, the coercivity decreases with decreasing crystallite size of nanopowder. The lowest coercivity was 7.8 Oe, which was obtained from the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanopowder sample synthesized at precursor concentration of 0.3M. Then, the crystallite size of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles was 8.8 nm.*

**Keywords :** -Fe<sub>2</sub>O<sub>3</sub>, Nanoparticles, Chemical vapor condensation, Superparamagnetic behavior, Iron acetylacetonate

### 1. Introduction

$\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles have been focused on their typical magnetic property represented by superparamagnetism, and technological applications to magnetic fluids, catalysts, high-density magnetic recording media, drug delivery system and hyperthermia [1,2]. Though various gas phase synthesis methods, such as spray- and laser pyrolysis, microwave plasma, and wire explosion, have been applied to synthesis of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, the relation between powder properties and process variable is still obscure, because particle behavior in gas phase is too unpredictable to be elucidated [3].

Chemical vapor condensation (CVC) has been described as a very convenient process for the synthesis of ceramic nanoparticles, since it has a simple structure. In this respect, we set our sight on the synthesis of highly dispersed iron oxide nanoparticles by CVC process and understanding the effect of process variables on the changes of microstructural and magnetic properties. First, we investigated the influence of temperature on crystal phase of iron oxide nanoparticles. Second, the effects of precursor concentration on the mean size, agglomeration, and magnetic properties of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were examined.

### 2. Experimental and Results

CVC process consisting of three parts, precursor evaporator, hot wall reactor, and powder collector, was designed for the synthesis of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. As a precursor, iron acetylacetonate, (Fe(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub>, Sigma-Aldrich Co., 99.9%), the most common  $\beta$ -diketonate

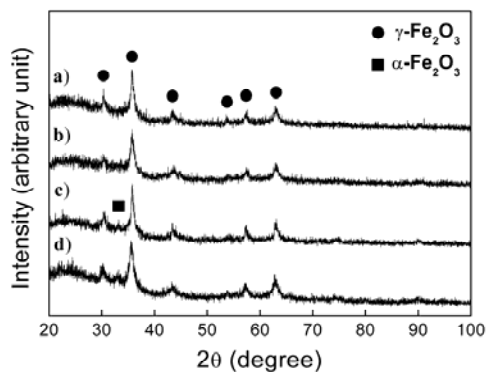
compound which is inexpensive, nontoxic and chemically stable at room temperature was used. First, precursor was carried to the evaporator and then heated to 220°C isothermally to generate stable precursor vapor. The evaporated precursor was then delivered into the reactor furnace by He carrier gas at a flow rate of 2 l/min, while the pressure in the reactor was held at 50 mbar. Simultaneously, the reaction gas, O<sub>2</sub> was fed into the reactor at a flow rate of 3 l/min.

Reaction temperature was changed in the range of 700–1000°C and precursor concentration was varied from 0.1M to 1.0M. After completion of the synthesis, the nanoparticles were sampled at the collector site outside the reactor tube, where temperature was held at room temperature. Crystal phase and microstructure of the iron oxide nanoparticles were analyzed by XRD and TEM. The magnetic properties of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanopowder were measured by VSM.

XRD patterns in Fig. 1 show that crystal phase of powder is strongly dependent on reaction temperature. From the patterns, we can find that nanopowder samples synthesized at 700°C and 800°C, consisted of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phases. Otherwise, samples synthesized at 900°C and 1000°C showed the diffraction peaks corresponding to pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The crystallite size calculated by Scherrer formula for these two  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanopowder samples at 900°C and 1000°C were 12.7 nm and 13.3 nm, respectively.

From the XRD patterns for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles synthesized at precursor concentration range of 0.1–1.0M, it was found that all powder samples consisted of pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase. The crystallite size of powder decreased with decreasing precursor concentration. This result explains that the decrease of number concentration of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> vapor clusters per unit volume in reactor decreased collision rate

of  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles in CVC reactor [4]. However at concentration under 0.2M, the mean crystallite size of  $\gamma\text{-Fe}_2\text{O}_3$  nanopowder increased with decreasing precursor concentration. This result indicated that the organic compounds in gas phase from precursor and isopropyl alcohol might affect on the formation of agglomerates.

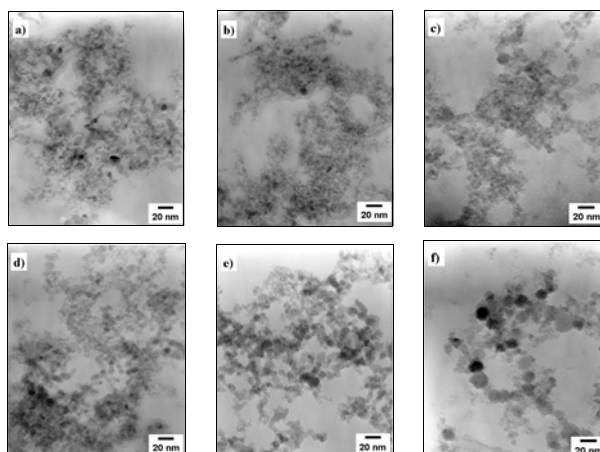


**Fig. 1. XRD patterns of iron oxides nanopowders synthesized at (a) 1000°C, (b) 900°C, (c) 800°C and (d) 700°C under pressure of 50 mbar.**

Figure 2 shows that the TEM micrographs of  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles synthesized at various precursor concentrations. It was observed that all nanoparticles were agglomerated and had a spherical shape regardless of precursor concentration. Though no significant difference in the degree of agglomeration was observed, the mean particle size measured from TEM micrographs increased with increasing precursor concentration in the range of 10–15 nm (Fig. 2(c)–(f)).

The magnetization versus magnetic field hysteresis curves at 300K showed that the coercivity ( $H_c$ ) of all powder samples was commonly lower than that of bulk  $\gamma\text{-Fe}_2\text{O}_3$  [5]. And it was found that  $H_c$  value decreased with lowering precursor concentration. In this point of view, this low coercivity is due to the superparamagnetism that magnetic particles with crystallite size below a critical limit show stable single domain behavior and significant changes in magnetic properties [6]. However at precursor concentration lower than 0.3M, the coercivity increased with decreasing precursor concentration.

This result was interpreted that increase of coercivity was due to the formation of agglomerates, which was considered as the evidence for our suggestion from XRD and TEM results explaining the formation of agglomerates from the effect of the residual organic compounds.



**Fig. 2. TEM micrographs of  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles synthesized at various precursor concentration, (a) 0.1M, (b) 0.2M, (c) 0.3M, (d) 0.4M, (e) 0.5M and (f) 1.0M.**

### 3. Summary

Nanoparticles of  $\gamma\text{-Fe}_2\text{O}_3$  phase were successfully synthesized by CVC process. It was found that  $\gamma\text{-Fe}_2\text{O}_3$  phase was obtained at temperature conditions above 900°C. In the precursor concentration range of 0.3–1.0M, crystallite size and mean particle size decreased with lowering concentration. Also, coercivity of nanopowders decreased with decreasing crystallite size, which showed superparamagnetic behavior. However, mean particle size and coercivity increased with decreasing precursor concentration at lower precursor concentration (0.1–0.2M).

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