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ScienceDirect
Journal of Magnetism and Magnetic Materials 310 (2007) 2393–2395
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Role of polyol in the synthesis of Fe particles

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Available online 30 November 2006

Abstract

Though there have been reports on the synthesis of Fe particles by using polyol process, the role of polyol has not been understood well and it still remains unclear. We report the successful synthesis of Fe nanoparticles in liquid polyols, their magnetic properties and also the influence of polyols for the formation of Fe nanoparticles. The oxide phase fraction and the magnetic properties are found to depend on the particle size of the Fe synthesized in various polyols like trimethylene glycol, propylene glycol and ethylene glycol.

PACS: 75.50.Bb; 75.50.Tt; 74.25.Ha

Keywords: Polyol process; Fe nanoparticle

1. Introduction

Among various chemical techniques available for the synthesis of metallic and alloy nanoparticles, polyol process stands out since the polyol medium prevents the particle from coming into contact with the oxidizing atmosphere. Though most of the transition metals were reduced successfully by polyol, the formation of iron in polyol is claimed only through disproportionation reaction of ferrous salts [1]. However, the formation of alloys such as FePt [2], FePd, FeCo, etc. were reported recently and cast a doubt on the disability of the polyol in reducing iron. Therefore, in this paper, we attempted the synthesis of Fe nanoparticles using polyol process and elucidate the role of polyol. The magnetic properties of the particles are also reported.

2. Experimental

The precursors used for the synthesis of Fe nanoparticles are $FeCl_2 \cdot 4H_2O$ and NaOH. The synthesis was attempted using polyols like trimethylene glycol (TMEG), propylene glycol (PG) and ethylene glycol (EG). The precursors were taken in a reaction vessel containing 100 ml of polyol and heated to the desired temperature with constant mechanical stirring. The synthesized samples were washed and stored in alcohol. The structure, morphology and magnetic properties of the particles were analyzed by X-ray diffraction (XRD) using a Cu target, scanning electron microscope (SEM) and vibration sample magnetometer (VSM).

3. Results and discussion

3.1. Synthesis of Fe in various polyols

The synthesis of Fe in polyols was attempted by reducing ferrous ions ($FeCl_2 \cdot 4H_2O$) in the presence of hydroxyl ion. The formation of the iron particles as a function of (a) type of polyol, (b) ferrous salts, (c) ferrous ion concentration, (d) hydroxyl ion concentration and (e) reaction temperature were studied in detail. However, this report will discuss the results pertaining to the Fe molar concentration of 0.02 M, OH/Fe ratio of 10 and reaction temperature of 393 K in different types of polyol. Fig. 1 shows the XRD pattern of the products synthesized in TMEG, PG and EG. Average grain sizes of the Fe nanoparticles synthesized in TMEG, PG and EG are 15, 23 and 32 nm, respectively, determined using Scherrer's formula. Depending on the

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doi:10.1016/j.jmmm.2006.10.1132

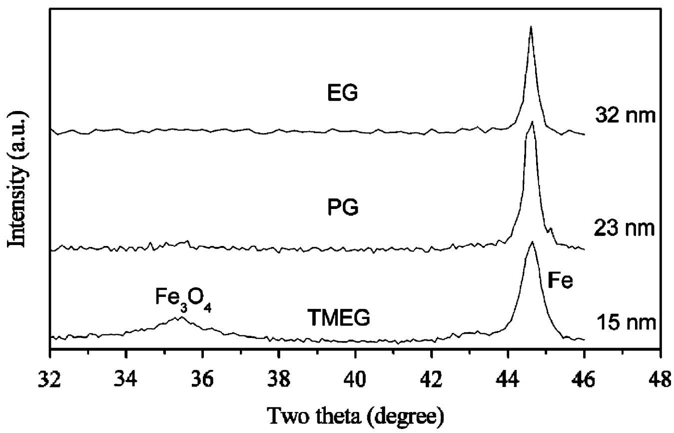

Fig. 1. XRD pattern of the Fe nanoparticles synthesized in various polyols.

reducing ability of the polyols, the yield of metal iron and iron oxide fraction in the product varied. The Fe_3O_4 fraction is the highest for the particles synthesized in TMEG, and almost no oxide peak is visible for the particles synthesized in EG as shown in Fig. 1. The particle size for the Fe synthesized in EG and TMEG are around 100 and 60 nm as observed from SEM and TEM (not shown), respectively. The larger particle size confirms that the particles are polycrystalline since the grain sizes observed from the XRD pattern are much smaller. The results suggest that the formation of oxides is due to the oxidation of iron and their fraction is related to the size of the nanoparticles. The highly reducing TMEG gives rise to the formation of smaller particles, which subsequently gets oxidized. On the other hand, the Fe particles synthesized in EG are large in diameter and the oxide fraction is below the detection limit of XRD. This has also been confirmed from the magnetic properties of the products. The saturation magnetizations for the particles synthesized in TMEG, PG and EG are 70, 82 and 126 $A\,m^2/kg$, respectively. The saturation magnetization is higher than that of magnetite nanoparticles (60 $A\,m^2/kg$) but less than that of bulk Fe (220 $A\,m^2/kg$). The magnetization value lower than the bulk is due to the distribution in the particle sizes with smaller particles getting converted to magnetite resulting in the reduction of magnetization. The yield and particle size of Fe synthesized in polyols varied depending on the reduction potential of the polyols. This suggests that the reaction mechanism for the formation of Fe nanoparticles in polyols is by reduction and not through disproportionation, where reaction does not depend upon the type of polyols. To confirm this further, we attempted the synthesis of iron particles in EG under various experimental conditions.

3.2. Synthesis of Fe in EG

As mentioned earlier, since the distribution of particles with smaller sizes would result in the oxidation of Fe, the reaction parameters such as OH^-/Fe ratio, temperature and heating rate were varied to obtain highly pure Fe particles. Among these, NaOH is found to play a major role in reducing any metal ion to metal atom. In the present case, the excess OH^- helps in reducing the reduction potential, E_h, of the species [3] as well as enhances the reaction rate by facilitating the formation of acetaldehyde. The XRD pattern of the product obtained under optimum conditions is shown in Fig. 2. Fig. 3 shows the typical SEM

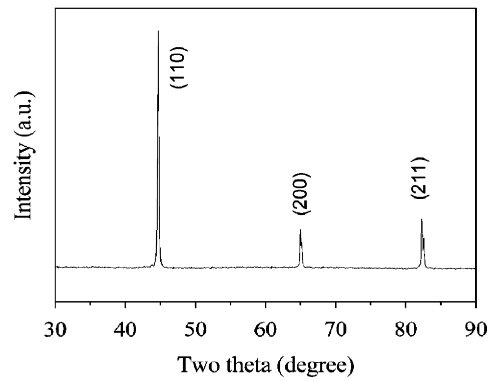

Fig. 2. XRD pattern of the Fe particles synthesized in EG.

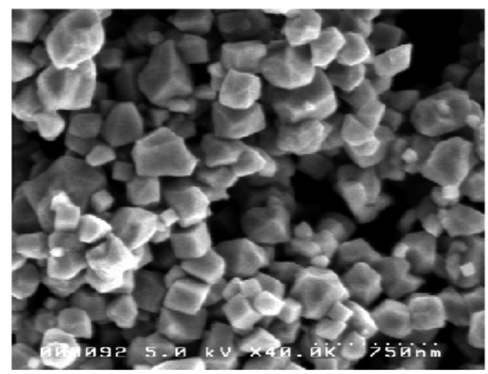

Fig. 3. SEM micrograph of sub-micron Fe particles synthesized in EG.

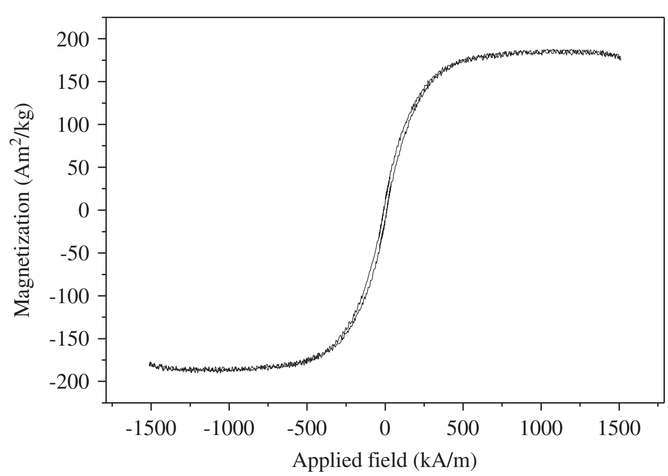

Fig. 4. Hysteresis loop at room temperature for the Fe particles synthesized in EG.

micrograph of Fe particles obtained above. The shape of the sub-micron size particles is found to be cubic. Fig. 4 shows the hysteresis loop at room temperature for the Fe particles synthesized in EG. The saturation magnetization of the particles is as large as $182.5\,\mathrm{A\,m^2/kg}$ suggesting that the oxide fraction was very low. The absence of magnetite, which should be present in equal amount in the case of disproportionation reaction, suggests that the particles are produced through the reduction of iron ions into metal as in the cases of reducing any other noble or transition metals.

4. Conclusion

We could conclude that the polyol acts as a reducing agent rather than a medium for the disproportional reaction as claimed earlier. The oxide peak appears in the Fe nanoparticles synthesized by polyol process due to the oxidation of smaller iron particles. The magnetic properties of the Fe nanoparticles are thus influenced by the particle size, where the smaller particles undergo oxidization and thereby the overall saturation magnetization is reduced. The synthesis of Fe at low temperatures will pave the way for Fe-based alloy nanoparticles such as FePt and FeCo with better magnetic properties at low temperatures.

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