Fabrication of core-shell Ti-containing silica encapsulating FePt particles as a spherical nanocatalyst

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Abstract. The encapsulation of fcc FePt nanoparticles (NPs) having a mean diameter of ca. 6 nm with the Ti-SiO₂ thick shell gives a new nanocomposite (FePt@Ti-SiO₂), which serves as an efficient nanocatalyst for the liquid-phase selective epoxidation. Recovery from the reaction mixture was readily attained by applying an external permanent magnet, and the spent catalyst could be recycled without any appreciable loss in activity.

1. Introduction

The development of promising catalysts with well-defined active structures that enable selective chemical transformations and can be completely separated is a paramount challenge [1]. It is widely accepted that the activity of a solid catalyst suspended in a liquid phase can benefit greatly from the use of smaller catalyst particles (< 1 µm) to avoid mass-transfer limitations [2]. However, the difficulties in recovering small particles from the reaction mixture severely circumvent their industrial applications, which can lead to blocking of filters and valves in chemical plants. Although nanoparticle-based catalysts possessing extremely large surface areas are also key components of catalytic activity [3-5], the separation step becomes a more troublesome issue as the size of the particles decrease to the nanometer scale.

With this in mind, we have developed Ti-containing silica (Ti-SiO₂) encapsulating superparamagnetic fcc FePt NPs (FePt@Ti-SiO₂). The inner magnetic FePt cores were shielded from the external environment by the impermeable coating, which prevents sintering and agglomeration of metal NPs under catalytic conditions. The catalytically active Ti-oxide moieties are located on the external surface of the coating and considered to be highly dispersed at the atomic level. This report describes the synthesis and characterization of the novel FePt@Ti-SiO₂ nanocomposite and its evaluation as a nanocatalyst for the oxidation of organic compounds using H₂O₂.

2. Experimental

2.1 The synthesis of FePt NPs: FePt NPs were prepared using standard airless techniques on a Schlenk line according to a procedure modified from that reported by Chen et al [6]. Platinum acetylacetonate (1 mmol, Pt(acac)₂, Wako Pure Chemical Ind., Ltd.) was mixed with 20 mL of dibenzyl ether (Tokyo Kasei Kogyo Co., Ltd) in a 200 mL three-neck flask. The mixture was degassed for 1 h and then heated to 120°C under Ar. Iron pentacarbonyl (2 mmol, Fe(CO)₅, Aldrich), 10 mmol of oleic acid (Wako Pure Chemical Ind., Ltd.), and 10 mmol of oleylamine (Aldrich) were then injected with mechanical stirring. The reaction mixture was heated at a rate of ~5°C/min to 310°C and...
maintained for 1 h. The black colored solution was allowed to cool to room temperature and NPs were precipitated with excess ethanol and collected by centrifugation. After washing several times with ethanol, the precipitate was uniformly dispersed in hexane. Elemental analysis confirmed that the average composition of the NPs was Fe₄₈Pt₅₂.

2.2 The ligand exchange procedure of the FePt NPs with (3-mercaptpropyl)-trimethoxysilane: (3-Mercaptpropyl)-trimethoxysilane (2 mL, 3-MPTS, Aldrich) was added to the 100 mL of hexane solution of as-synthesized FePt NPs (0.13 g). The mixture was stirred for 15 min, and precipitated with ethanol and collected by centrifugation. After washing several times with ethanol, the precipitate was stored in ethanol.

2.3 The synthesis of FePt@Ti-SiO₂: A 500 mL ethanol solution of the modified FePt NPs with 3-MPTS (0.05 g) was mixed with a 200 mL of ethanol solution containing tetraethyl orthosilicate (20 μL, TEOS, Wako Pure Chemical Ind., Ltd.) and tetrapropylorthotitanate (1 μL, TPOT, Wako Pure Chemical Ind., Ltd.). After stirring for 12 h at room temperature, the encapsulated particles were repeatedly centrifuged and washed using excess ethanol, giving a FePt@Ti-SiO₂.

3. Results and discussion

The synthetic procedure for the FePt@Ti-SiO₂ is illustrated in Figure 1. Uniformly distributed FePt NPs were synthesized by decomposition of Fe(CO)₅ and reduction of Pt(acac)₂ in the presence of oleic acid and oleylamine. Next, 3-MPTS was added to the hexane solution of as-synthesized FePt NPs and stirred. Ligand exchange with 3-MPTS made the FePt NPs dispersible in the alcoholic solution. Finally, precursors of Ti-SiO₂ (TEOS and TPOT) were added to the FePt NPs dispersed in ethanol and stirred. The use of 3-MPTS was motivated by the following reasons: 3-MPTS is soluble in alcoholic solvent and would readily bind to the surface of the metal particles via thiolate linkage. Furthermore, trimethoxysilane moieties facilitate formation of the Ti-SiO₂ phase by subsequent sol-gel polymerization.

![Fig. 1](image1.png)

**Fig. 1** Schematics of the procedure for the synthesis of FePt@Ti-SiO₂.

The intensities of the diffraction peaks in the XRD patterns (Cu Kα radiation) of the FePt@Ti-SiO₂ are low, presumably due to the smaller size of the particles. However, they exhibited clear peaks due to the fcc FePt around 40.0°, 46.7°, and 68.2°, corresponding to the (111), (200), and (220) reflections, respectively. Assuming that the FePt NPs are spherical in shape, the average crystalline size after encapsulation was calculated to be 5.9 nm by applying Scherrer’s equation for the (111) reflection.

**Figure 2** shows a typical TEM image of the core-shell FePt@Ti-SiO₂. These spherical particles have 45–50 nm thick Ti-SiO₂ shell that were formed by TEOS and TPOT with FePt NPs. Each Ti-SiO₂ sphere encapsulates one FePt NPs, although a small fraction of the particles possess either two or zero FePt NPs. The average diameter ($d_{ave}$) of FePt

![Fig. 2](image2.png)

**Fig. 2** TEM image of FePt@Ti-SiO₂.
NPs were determined to be ca. 6 nm. This observation is consistent with the results of XRD analysis, as described earlier, verifying the single-crystalline nature of the particles.

The magnetic properties were investigated using a SQUID magnetometer. As shown in Figure 3, the isothermal magnetization curve of the FePt@Ti-SiO₂ at 300 K displayed a rapid increase with increasing applied magnetic field, due to superparamagnetic relaxation [7]. This indicates that the thermal energy can overcome the anisotropy energy barrier of the individual particles, and the net magnetization of these nanoparticle assemblies is zero in the absence of an external field. Hysteresis was absent with zero remanence ($M_r$) and coercivity ($H_c$), and the saturation magnetization ($M_s$) reached up to 0.58 emu/g for FePt@Ti-SiO₂. With decreasing temperature, the magnetization of both samples increased and exhibited a symmetric hysteresis loop at 5 K ($M_r = 0.44$ emu/g, $H_c = 750$ Oe), indicating a transition from superparamagnetic to ferrimagnetic behavior.

Figure 4A shows the Ti K-edge XANES spectra of the FePt@Ti-SiO₂, Ti(OiPr)₄, and TiO₂ powder (P25: anatase 80%, rutile 20%). The spectrum for TiO₂ powder shows several well-defined pre-edge peaks attributable to the anatase TiO₂ in a symmetric octahedral environment [8]. On the other hand, the FePt@Ti-SiO₂ and Ti(OiPr)₄ were found to exhibit an intense single pre-edge peak due to the lack of an inversion center in the regular tetrahedron structure [8]. Observation of this intense single pre-edge peak indicates that the Ti-oxide moieties in the FePt@Ti-SiO₂ have tetrahedral coordination [9]. The FT-EXAFS data (Figure 4B) shows a peak suggestive of a contiguous Ti–O–Ti bond for the TiO₂ powder. On the other hand, the FePt@Ti-SiO₂ showed only a strong peak at around 1.6 Å, which could be assigned to the neighboring oxygen atoms due to a Ti–O bond.

Fig. 3 Field-dependent magnetization curve for FePt@Ti-SiO₂ measured at 300 K (■) and 5 K (○).

Fig. 4 (A) Ti K-edge XANES spectra and (B) FT-EXAFS spectra for (a) FePt@Ti-SiO₂, (b) Ti(OiPr)₄, and (c) TiO₂ powder (P25).
We explored the catalytic ability of the FePt@Ti-SiO2 in the epoxidation of cyclooctene using 30% hydrogen peroxide as a simple test reaction. Results of this reaction indicated that the corresponding cyclooctene oxide was obtained in >99% selectivity and the turn over number (TON) based on Ti approached 48 after 24 h (Table 1). More important advantage of the FePt@Ti-SiO2 is the facile recovery from the reaction mixture and the high reusability. Upon completion of the oxidation reaction, the magnetic properties of the FePt@Ti-SiO2 can afford a straightforward means to isolate the catalyst from the colloidal solution. By applying an external permanent magnet, the catalyst was attracted. The recovered catalyst could then be recycled in the epoxidation of cyclooctene at least three times while maintaining identical inherent activity to the initial run.

Table 1. Oxidation of cyclooctene using FePt@Ti-SiO2 and recycling experiment

| Run | 1st | 2nd | 3rd | 4th |
|-----|-----|-----|-----|-----|
| TON | 48  | 48  | 48  | 48  |
| Select. / % | >99 | >99 | >99 | >99 |

4. Concluding remarks
A novel spherical nanocatalyst, FePt@Ti-SiO2, was synthesized by adopting a two-step coating method via a ligand exchange and a sol-gel process. Our designed architecture enabled the powerful combination of useful functionality, superparamagnetism that was attracted to a magnetic field, as well as a catalytically active site that exhibited prominent performance for specific catalytic reactions. The present strategy provides great flexibility in the selection of the magnetic core, as well as catalytically active center. Introduction of these features into nanoparticulate systems enables achievement desired superparamagnetic response as well as particular catalytic reactions.

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