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Heterostructured zero valent iron–montmorillonite nanohybrid and their catalytic efficacy

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ABSTRACT

Nanohybrid catalysts that comprised montmorillonite (Mt) matrix and embedded zero-valent Fe nanoparticle are presented. In this process, clay particles are used as 2-dimensional template that induce the growth of intercalated nanomaterials. Fe polycations are first embedded within the interlayer space and then reduced to Fe nanoparticles through thermal annealing in reducing atmosphere. Structural studies using electron microscopy and high energy X-ray show that the intercalated status of the polycations dictates the crystal structure, shape and size of final Fe compound particles. The magnetic property and caltalytic efficacy of hybrid particles have been verified using magnetometer measurement and Fenton reaction. Hybrized α-Fe nanoparticles show high magnetization inherent to zero valent Fe, and high catalytic efficacy in decomposing Rhodamine B due to their zero valency and large surface areas. This simple synthesis process of stable iron nanoparticle without organic agents will be beneficial for large scale production of highly effective catalysts exploiting controlled phase and shape of embedded nanoparticles.

1. Introduction

The synthesis of iron nanoparticles with controlled phase and size has attracted a great amount of scientific and technological interests due to catalytic effects and magnetic properties. In particular, maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4) and zero valent iron (Fe_0) nanoparticles have been intensively studied (Ahang et al., 2009; Cowburn and Welland, 2000; Huber, 2005; Shevchenko et al., 2006). When these nanoparticles are coated with a proper surface layer such as silica and hydrophilic polymer, these magnetic particles can be dispersed into liquid media to form colloidal dispersions for environmental and medical applications (Fu et al., 2001; Garrido-Ramírez et al., 2010; Gonzales and Krishnan, 2007; Lu et al., 2002; Yu et al., 2006).

Among the iron based nanoparticles, zero valent Fe is effective redox agent for in-situ remediation of organic and inorganic pollutants (Bang et al., 2005; Garrido-Ramírez et al., 2010). Also, their particle dispersions have been widely explored for magnetorheological fluid, bio molecule separation, and magnetic resonance image contrast agent due to their sensitive response to magnetic field (Raj and Moskowitz, 1990). However, synthesizing iron nanoparticles with high magnetization and controlled configuration, and suppressing their agglomeration in solutions still remain challenging, which necessitates a minimization of the surface energy. Currently, electrochemical method and passivation of organic molecules on the iron particle surface size are used to tailor the size and shape of iron nanoparticle (Chen et al., 2009). An alternative solution to overcome is found in the recent studies on the intercalated clays. Metal oxide nanoparticle such as Al_2O_3, ZrO_2, TiO_2, ZnO, SiO_2–Fe_2O_3, and SiO_2–TiO_2 and SiO_2–CoO were successfully confined to the interlayer space to form pillared interlayer clays (PILC) to increased active surface area for the enhanced catalytic properties (Choy et al., 2002; Hur et al., 2006; Jang et al., 2005). Recently, we have also demonstrated pillared iron oxide-clay hybrid particles which show stable dispersion in the aqueous and prevent agglomeration of individual iron oxide particles (Son et al., 2010). However, the synthesis of nanosized zero valent Fe by using the clay particles has been rarely reported.

In this study, iron pillared montmorillonite (FePMt) was successfully synthesized through the intercalation and the thermal treatment in a reducing ambient. We have carried out the systematic characterizations of crystal structure and physicochemical properties of the resulting nanohybrids using X-ray diffraction (XRD), elemental analysis and N_2 adsorption–desorption isotherm measurement. X-ray absorption spectroscopic (XAS) analysis has been employed to probe the local crystal structure of this nanohybrid material. Moreover, the magnetic property and catalytic efficacy of hybrid particles have been verified using magnetometer measurement and Fenton reaction.

2. Experimental

2.1. Material and chemicals

Na^+-montmorillonite (Kunipia F, Kunimine Corp) was used as a starting clay mineral with the chemical formula of $Na_{0.35}K_{0.01}Ca_{0.02}(Si_{3.89}Al_{0.11})-(Al_{1.60}Mg_{0.32}Fe_{0.08})O_{10}(OH)_2\cdot nH_2O\cdot FeCl_3\cdot 6H_2O$

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(Aldrich, 97%). NaOH (Mallinckro) was used to synthesize polycation precursors.

2.2. Synthesis and characterization

Fe polycations were produced by reacting a 0.2 mol $FeCl_3$ and a 0.4 mol NaOH in DI water (1 L) at 25 °C or 70 °C. Then, 0.07 mol polycations were added to a 100 ml aqueous dispersion of 1 wt.% montmorillonite (Mt) particles FePMt particles were collected by centrifugation, were washed thoroughly with deionized water several times, and were freeze-dried to remove residual water. To convert iron polycations to iron species, a part of dried particles were annealed in H_2 and Ar mixture gas at 300, 400, and 550 °C. X-ray diffraction (XRD) measurements of synthesized particles were carried out using Cu Kα radiation ($\lambda = 1.54184$ Å) (Philips PW 1810 diffractometer). X-ray adsorption near edge spectroscopy (XANES) analysis was carried out by X-ray adsorption spectra (XAS) experiments for the Fe K-edge with the beam line 7C at the Pohang Light Sources in Korea. XAS data were collected at room temperature in a transmission mode using gas-ionization detectors. All the spectra were calibrated carefully by using the reference spectrum of Fe metal. Data analysis for the experimental spectra was performed with a standard procedure, as reported previously (Choy et al., 1997, 1998, 2000). Nitrogen adsorption and desorption isotherm was measured at liquid nitrogen temperature by using a Thermoquest Sorptomatic 1990. Before the adsorption measurements, the samples were outgassed under vacuum for 3 h at 100 °C. Magnetization of the hybrid materials was measured with a vibrating sample magnetometer (LakeShore 7400). Element analyses were carried out using an inductivity coupled plasma (ICP) method (Thermo, ICAP 6000). For ICP analysis, the samples were melted with lithium metaborate at 900 °C in 30% HNO_3. To measure the catalytic performance of zero valent FePMt particles, FePMt particles containing a 0.35 mmol Fe were introduced into 50 ml of a 5 mg/l Rhodamine B (RhB) solution in a 200 ml glass cell with a water cooling jacket outside. Air was bubbled into the RhB solution during the Fenton reaction. As a comparison, the catalytic properties of 0.35 mmol commercial Fe_0, Fe_3O_4 and Fe^{3+} were conducted under the same conditions, respectively. The concentration of RhB was monitored by a UV–vis spectrometer (Perkin Elmer, Lambda 35) at every 10 min.

3. Results and discussions

Fig. 1 shows XRD patterns of pristine Mt particles and Mt particles intercalated with Fe polycations at different temperature. The (*00l*) reflections of intercalated sample are found at lower 2θ than those of pristine Mt, which indicates that Fe polycations were intercalated into Mt particles. In constrast, the basal distance of pristine Mt along c-axis was 0.96 nm. The basal distance of intercalated particles was calculated to be 1.47 nm for 25 °C aged iron polycations and 1.96 nm for 70 °C aged Fe polycations.

After the intercalated particles were thermally annealed in Ar + 5%H_2 atmosphere, we denoted particles as FePMt-X–Y. X and Y represent the aging temperature of Fe polycations and the annealing temperature of the hybrid particles, respectively. XRD patterns of FePMt show several peaks resulting from Fe metal and iron oxides. The relative ratio of metal and oxide components depends on annealing temperature and atmosphere. In Fig. 2, the reflections of FePMt-25–300 at $2\theta = 33.2^\circ$, 35.7°, 40.98°, 62.6° and 64.2° are identified as the diffraction peaks of hematite (α-Fe_2O_3) phase (Deng et al., 1989). In FePMt-70–300, additional XRD peaks corresponding to magnetite (Fe_3O_4) phase are found at $2\theta = 30.24^\circ$, 35.7°, 43.1° and 62.6° in addition to those of α-Fe_2O_3. This indicates that the intercalation at 70 °C reduces the amount of oxygen in the lattice more than the intercalation at 25 °C. The ratio of α-Fe_2O_3 and Fe_3O_4 is estimated by comparing the intensities of their XRD peaks (Gavíria et al., 2007). In the hematite, two strongest peaks, (*104*) reflection at 33.2° and (*110*) reflection at 35.7° have same intensity. However, (*313*) reflection at 35.7° has the largest intensity in the magnetite. As a reference sample, a mixture of α-Fe_2O_3 (50 wt.%) and Fe_3O_4 (50 wt.%) was also examined. The inset of Fig. 2 shows that the intensity ratio of peaks at 33.2° and 35.7° is about 1:1.6. In XRD pattern of FePMt-70–300, the ratio of same peaks is approximately 1:2. This indicates that the amount of the magnetite in FePMt-70–300 is much more than 50%. In contrast, reflections at 33.2° and 35.7° have almost same intensity in FePMt-25–300, which suggests that the hematite is mainly produced in 300 °C annealing of 25 °C-intercalated Mts.

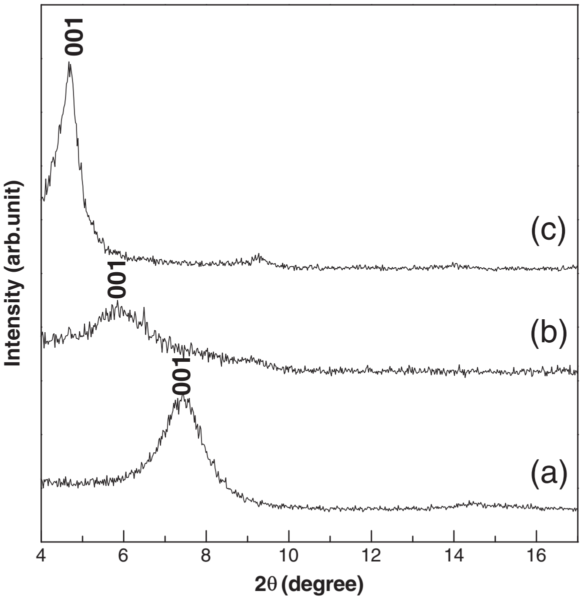

Fig. 1. XRD patterns of (a) pristine clay and expanded interlayer space after intercalating iron oxide precursor at synthesizing (b) 25 °C and (c) 70 °C.

The magnetite phase is clearly observed in both FePMt-25–400 and FePMt-70–400 (Fig. 2(b) and (f)). In addition, the (*110*) peak of α-Fe starts to appear in FePMt-70–400. After 500 °C annealing, a main phase changes to α-Fe and only a small trace of (*313*) reflection of the magnetite is found in FePMt-70–500 (Fig. 2(g)). In contrast, a main phase of FePMt-25–500 that is annealed at 500 °C is still Fe_3O_4. After being annealed at 550 °C, the partial reduction of Fe_3O_4 to α-Fe is show at 550 °C annealed condition, but its main phase is still Fe_3O_4 (Fig. 2(c) and (d)).

The effect of the location of the Fe compound nanoparticles on the phase transition is supported by two-step annealing synthesis as shown Fig. 3. Hybrid particles were annealed first at 400 °C in N_2 atmosphere and then subsequently annealed at 550 °C in Ar + 5% H_2 atmosphere. Regardless of the polycation synthesis temperature, the Fe polycations are fully crystallized to α-Fe_2O_3 by the first annealing at 400 °C in N_2. When these samples are subsequently annealed in Ar and 5% H_2 at 550 °C, however, the crystal structure of the Fe compounds in the hybrid particles depends on the type of Fe polycations. In the particles intercalated with 25 °C aged Fe polycations, the reflections of only Fe_3O_4 phase were observed. In contrast, the hybrid particles intercalated with 70 °C aged Fe polycations were partially transformed to α-Fe. The transformation of α-Fe_2O_3 to Fe_3O_4 or α-Fe requires the reducing reaction of Fe^{3+} in the surface of α-Fe_2O_3. Therefore, the result of the two-step annealing indicates that the intercalation of Fe polycations at 70 °C leads to the suppressed growth of nanoparticles in subsequent annealing process. This is consistent with XRD patterns in Fig. 2, which proves enhanced insertion of Fe polycations into the interlayer space in 70 °C process.

These differences in the crystal structure of Fe compounds of the annealed hybrid particles used 25 °C and 70 °C polycation suggest that stable polycation species at 70 °C are easily intercalated into the interlayer space. Once Fe compound nanoparticles are immobilized between the layers of the Mt particles, the growth of the nanoparticles is