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Preparation of alumina–iron oxide compounds by gel evaporation method and its simultaneous uptake properties for Ni^{2+}, NH_4^+ and $H_2PO_4^-$

Fahmida Gulshan, Yoshikazu Kameshima, Akira Nakajima, Kiyoshi Okada*

Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152-8552, Japan

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ABSTRACT

Fe_2O_3/Al_2O_3 powders with a range of Fe/Al compositions were prepared by a gel evaporation method to investigate the effect of alumina on the product phases, magnetic properties and simultaneous adsorption of Ni^{2+} (a model heavy metal cation), NH_4^+ (a model eutrophication-related cation) and $H_2PO_4^-$ (a model harmful anion). Precursor gels were prepared by dissolving $Fe(NO_3)_3{\cdot}9H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ in ethylene glycol, evaporating to dryness, grinding and heating at 300–1000 °C for 5 h. The crystalline products were γ-Fe_2O_3 (maghemite), formed at 300–600 °C, or α-Fe_2O_3 (hematite) and $AlFeO_3$, formed >600 °C. The temperatures of the phase change from γ-Fe_2O_3 to α-Fe_2O_3 increased with increasing alumina additions. The resulting lattice parameters suggest that Al^{3+} is incorporated into these phases up to about 15 mol.% at 300 °C, falling to 11 mol.% in the γ-Fe_2O_3 formed at 600 °C. The α-Fe_2O_3 formed at 700 °C contained 6 mol.% Al, increasing to 14 mol.% at 1000 °C. The magnetic properties of the samples were measured using a vibrating sample magnetometer. The saturation magnetization values of the γ-Fe_2O_3-containing samples increased with the addition of alumina to a maximum value of 61 emu/g in the sample containing 95 mol.% Fe_2O_3 heated at 400 °C. The simultaneous adsorption of Ni^{2+}, NH_4^+ and $H_2PO_4^-$ from water was investigated by a batch method. The highest adsorption values were found for the sample containing 80 mol.% Fe_2O_3 heated at 600 °C, which contained both γ-Fe_2O_3 and α-Fe_2O_3. It was therefore concluded that the addition of alumina to iron oxide affects the crystalline phases and phase changes, and enhances the simultaneous cation and anion uptake ability of the materials.

1. Introduction

Recently, the pollution of wastewater and surface water by toxic ions has become a severe environmental problem. The vast majority of toxic ions are waste products of various industrial processes, especially the effluent from electroplating plants, metal finishing operations, mining and mineral processing, oil refining and extractive metallurgy processes. Contamination of water is principally by two types of ions, namely, heavy metal ions, and ions such as ammonium and phosphate which cause eutrophication. A variety of methods have been used to remove toxic ions from water and wastewater, arising from many years of development of absorption technology. Many different adsorbents for wastewater treatment have been commercialized or are being developed [1]. For instance, zeolites and layered double hydroxides (LDHs) are excellent sorbents for cations and anions, respectively, but compounds capable of simultaneously absorbing both cations and anions are preferable for practical use [2]. Previously the effectiveness of amorphous CaO–Al_2O_3–SiO_2 (CAS) [3] and CaO–Fe_2O_3–SiO_2 (CFS) compounds [4] for simultaneous uptake of both cations and anions has been reported. Such simultaneous ion uptake is thought to be due to a combination of three chemically different components, i.e. the anion exchange property of CaO, the amphoteric properties of Al_2O_3 and Fe_2O_3, and the cation exchange property of SiO_2.

Fe- and Al-hydroxides and oxides are well known to show high uptake of anions [5], especially toxic oxyanions such as arsenate [6,7] and phosphate [8–10]. Chubar et al. [11] synthesized $Fe_2O_3{\cdot}Al_2O_3{\cdot}xH_2O$ with high specific surface area (c.a. 400 m^2/g) by a hydrothermal method; this product showed good uptake of phosphate ions. Tanada et al. [12] investigated adsorption characteristics of phosphate onto aluminium oxide hydroxide from seawater. Hu et al. [13] showed that nanosize maghemite (γ-Fe_2O_3) was very effective in adsorbing Cr^{6+}, Cu^{2+} and Ni^{2+} from wastewater. Li et al. [14] synthesized Fe_2O_3–Al_2O_3 compounds by coprecipitation and investigated their photocatalytic functions. The highest photocatalytic decomposition rate of bisphenol A was found in the compound of 90 mol.% Fe_2O_3 composition, illustrating the effect of Al^{3+} incorporation. El-Sharkawy et al. [15] prepared Fe_2O_3–Al_2O_3 compounds by coprecipitation and examined their catalytic activity, reporting that the texture, acidic properties and catalytic activity depended on the thermal treatment and Fe_2O_3/Al_2O_3 ratios of the compounds. It is therefore of interest to investigate the effect of Al^{3+} substitution

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* Corresponding author. Tel.: +81 357342524; fax: +81 357343355.
E-mail address: okada.k.ab@m.titech.ac.jp (K. Okada).

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for Fe_2O_3 in the Fe_2O_3–Al_2O_3 system on the simultaneous uptake of ions by these compounds. Moreover, some phases of iron oxide have good magnetic properties, suggesting the possibility of combining their adsorption properties with the magnetic separation of harmful components from a polluted system by applying a simple magnetic field. This could replace the common technology of filtration and centrifuge separation, and after magnetic separation, the harmful components could be easily removed from the magnetic particles that could then be reused.

In this study, Fe_2O_3–Al_2O_3 compounds with various Fe/(Fe + Al) molar ratios were synthesized by a gel evaporation (GE) method [16] and tested for the simultaneous removal of harmful ions from wastewater. Here, Ni^{2+} was used as the model for heavy metal ions, NH_4^+ the model for ions implicated in eutrophication and $H_2PO_4^-$ the model for harmful oxyanions. To determine the feasibility of magnetic separation of these compounds, their magnetic properties were also measured. Thus, the objective of this study was to examine the effect of Al_2O_3 additions on the compounds formed, their magnetic properties and their simultaneous adsorption of cations and anions, and also to assess the performance of Fe_2O_3–Al_2O_3 compounds for the simultaneous removal of harmful ions from contaminated water considering as a candidate material for low cost, harmless and high efficiency simultaneous removal of harmful ions.

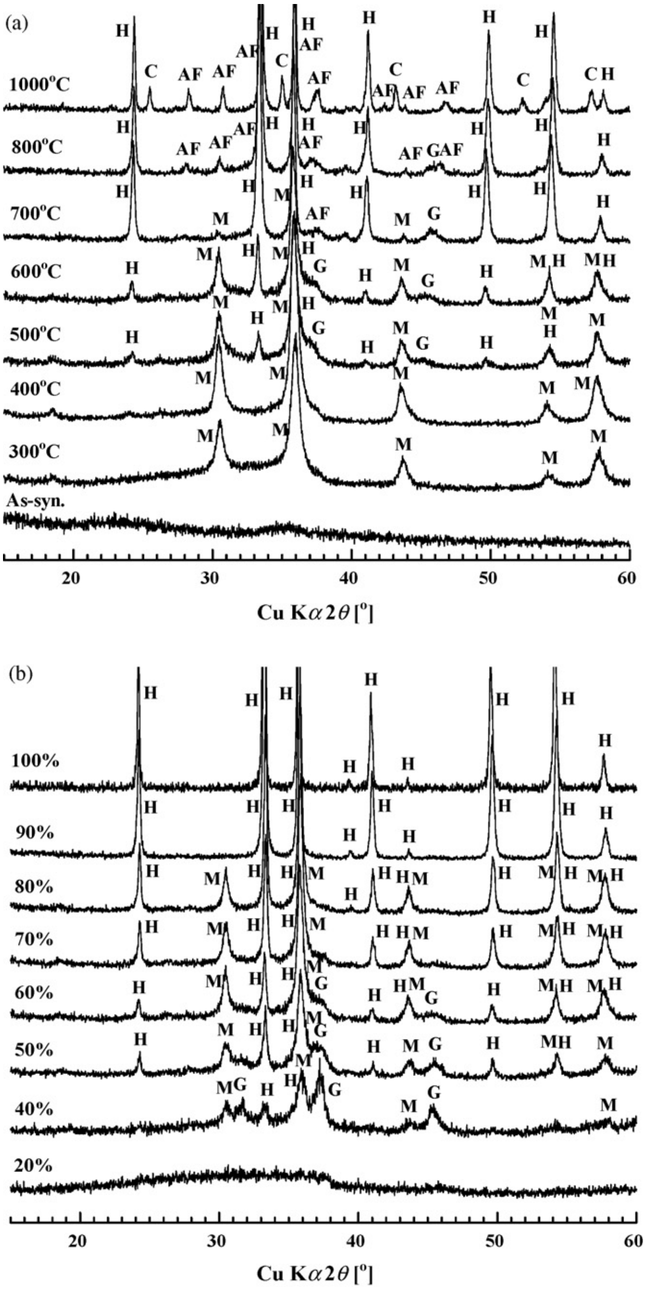

Fig. 1. XRD patterns of (a) samples containing 60 mol.% Fe_2O_3 heated at various temperatures, (b) samples heated at 600 °C with various Fe/(Fe + Al) ratios. Key: AF = $AlFeO_3$, C = α-Al_2O_3, G = γ-Al_2O_3, H = α-Fe_2O_3 and M = γ-Fe_2O_3.

2. Experimental

2.1. Synthesis of the samples

Fe_2O_3–Al_2O_3 compounds were synthesized by the Pechini process [16] using metal nitrates and ethylene glycol as the starting materials, described here as the gel evaporation (GE) method. The starting materials (ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$ and aluminium nitrate $Al(NO_3)_3 \cdot 9H_2O$) were dissolved in ethylene glycol at a molar ratio of (total metal nitrates):(ethylene glycol) = 1:3 with the addition of a minimum volume of water to dissolve the nitrates. The resulting solution was warmed on a hotplate stirrer at 90 °C to evaporate the solvents, after which the nitrate–glycol mixture auto ignited, producing voluminous foam and finally yielding a loose powder. The powders were dry-ground in a planetary ball mill (LAPO-1, Ito Seisakusho Ltd., Japan) using a Si_3N_4 pot with 30 Si_3N_4 balls (5 mm ϕ) at 300 rpm for 3 h with a ball: sample mass ratio of 30:1. After grinding, the samples were calcined at 300–1000 °C in air for 5 h at a heating rate of 10 °C/min. In this way, samples containing 0, 20, 40, 60, 70, 80, 90, 95 and 100 mol.% Fe_2O_3 were prepared.

2.2. Characterization methods

X-ray powder diffraction (XRD) patterns were obtained (XRD-6100, Shimadzu) using monochromated Cu Kα radiation (40 kV to 30 mA). The lattice parameters of the crystalline phases were calculated by the least-squares method. The specific surface area (S_{BET}) of the samples was determined by a multipoint BET method using N_2 as the adsorbate (Autosorb-1, Quantachrome). The magnetic properties were determined using vibrating sample magnetization (VSM) equipment (BHV-50H, Riken Electronics) with a powder cell.

2.3. Uptake experiments

Simultaneous uptake of Ni^{2+}, $H_2PO_4^-$ and NH_4^+ was determined at room temperature for 24 h by a batch method using a solution containing 8 mM each of $NiCl_2 \cdot 6H_2O$ and $NH_4H_2PO_4$. The sample/solution ratio was fixed at 0.1 g/50 ml. The pH was measured immediately prior to placing the sample into the solution (initial pH) and after the reaction (final pH). After the uptake experiments, the samples were filtered, washed 3 times with distilled water and dried at 80 °C overnight. The concentrations of Ni^{2+}, $H_2PO_4^-$, Fe^{3+} and Al^{3+} before and after the experiments were analyzed by ICP-OES (Prodigy, Leeman Labs.) while the NH_4^+ concentration was determined by ion chromatography (IA-200, TOA-DKK). The uptake % and uptake (mmol/g) were calculated using the following formulas:

$$\text{uptake (mmol/g)} Q_0 = \frac{(C_i - C_f)V}{M}$$

$$\text{uptake \%} = 100\frac{C_i - C_f}{C_i}$$

where C_i, C_f, V and M are the initial concentration (mmol/L), final concentration (mmol/L), volume of solution (L) and mass of sample (g), respectively.