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Simultaneous uptake of Ni^{2+}, NH_4^+ and PO_4^{3-} by amorphous $CaO–Al_2O_3–SiO_2$ compounds

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Abstract

Simultaneous uptake of Ni^{2+}, NH_4^+, and PO_4^{3-} by amorphous $CaO–Al_2O_3–SiO_2$ (C-A-S) compounds was investigated using batch and column methods. Fifteen different C-A-S samples with systematically varied chemical compositions were prepared by coprecipitation from ethanol–water solutions containing $Ca(NO_3)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, and $Si(OC_2H_5)_4$, using NH_4OH as the precipitating agent. The resulting precipitates were dried and heated at various temperatures to produce the C-A-S samples, which were then characterized by XRD, FTIR, solid state MAS NMR, DTA-TG, and N_2 adsorption. All the C-A-S samples prepared at 600–900 °C were amorphous, apart from the CaO-rich samples. Simultaneous uptake of Ni^{2+}, NH_4^+, and PO_4^{3-} was determined by a batch method using a solution with an initial concentration of 2 mM. In these experiments, the uptake abilities of the C-A-S samples for Ni^{2+} and PO_4^{3-} were high, but were relatively low for NH_4^+. The uptake abilities for Ni^{2+} and PO_4^{3-} increased but that for NH_4^+ decreased as the silica content in the C-A-S decreased, suggesting that similar uptake mechanisms (ion substitution and/or precipitation) are operating for Ni^{2+} and PO_4^{3-}, but the uptake mechanism for NH_4^+ is different (physical adsorption). The column experiments indicate that the order of uptake ability of C-A-S for the three ions is $NH_4^+ \ll PO_4^{3-} < Ni^{2+}$. Although the silica content of the C-A-S does not have the expected influence on the uptake of these three ions, for NH_4^+ it plays an important role in the formation of the amorphous phase and also in the suppression of Ca^{2+} and/or Al^{3+} release from the C-A-S during the uptake experiments. The optimum uptake properties of the C-A-S can thus be controlled by adjusting the chemical compositions and heating conditions under which the samples are prepared.

Keywords: Simultaneous uptake; Calcium aluminosilicate; Heavy metal ion; Phosphate ion; Ammonium ion

1. Introduction

Increases in population and human activity have led to a world increase in the volume and change in the type of waste matter being generated, strongly influencing the environment, e.g., by the release of toxic combustion gases and aerosols to the atmosphere, by dissolution of toxic ions in water, and by precipitation of toxic ions in the soil. It is therefore important to reduce the amount of waste generated, to reduce its volume by careful firing, and to solidify the solid into an environmentally inert material. It would be of even greater benefit if the solidified material had environmental protection properties, for example, the ability to adsorb toxic molecules and ions.

Based on these considerations, we have investigated the development of environmentally functional materials from wastes. Glass ceramics for use as building materials have been prepared from wastes such as Kira (the silica-rich waste byproduct of the beneficiation of silica sand), plastic clay, and paper sludge ash [1]. Activated carbons prepared by chemical activation of old paper have been found to have high specific

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surface areas and good sorption properties [2], while physical activation generates a product that maintains the original paper shape [3]. Paper sludge was found to show good uptake ability and high selectivity for various heavy metal ions in solution if carefully heat-treated to form an amorphous phase rather than crystalline phases [4,5]. Thus, this is a potentially very useful environmentally functional material, with applications similar to those of artificial zeolites synthesized from fly ash [6–8] and bauxite refinery residues (Bauxsol) [9], which are used to improve water quality by removing toxic cations and anions.

All these wastes (e.g., paper sludge, coal fly ash, sewage ash, incinerator ash, blast furnace slag, steel making slag) contain as their major constituents the oxides CaO, Al_2O_3 (Fe_2O_3), and SiO_2. It is therefore of interest to examine the sorption properties of compounds in the CaO–Al_2O_3–SiO_2 system in which the chemical composition is systematically varied. In practice, such compounds would preferably be prepared by mixing and calcining these various wastes. As a starting point, however, we will first prepare the target compounds from chemical reagents by coprecipitation.

In this paper, a systematic series of amorphous CaO–Al_2O_3–SiO_2 compounds (C-A-S) were prepared with a range of CaO:Al_2O_3:SiO_2 ratios and their simultaneous uptake abilities were determined for Ni^{2+} (a representative heavy metal ion), NH_4^+, and phosphate ions (the ions responsible for eutrophication). The uptake studies were made using both batch and column methods.

2. Materials and methods

2.1. Preparation

C-A-S xerogels of various compositions were prepared by coprecipitation. The starting materials were reagent-grade calcium nitrate tetrahydrate, aluminum nitrate nonahydrate, and tetraethyl orthosilicate (TEOS). The xerogels were prepared according to the experimental flow chart shown in Fig. 1. The total concentration of starting materials was adjusted to 1.2 M and the total amount of ethanol solution was 200 ml in all the preparations. After the solution was stirred for 2 h, 25 mass% aqueous ammonia solution (200 ml) was added rapidly to the solution with vigorous stirring. The precipitates were immediately recovered using an evaporator at 60 °C for 1 h and subsequently dried at 110 °C for 48 h in an oven. The xerogels were then heated at 600–1000 °C for 17 h. The resulting samples are described in terms of their oxide composition CaO:Al_2O_3:SiO_2 = a:b:c (mass ratio) and heating temperature d, thus, abc-d.

2.2. Characterization

The heated samples were examined by X-ray powder diffraction (XRD), thermal analysis, solid state MAS NMR, and N_2 gas adsorption. XRD measurements were performed using a diffractometer (XRD-6100, Shimadzu) with monochromated CuK_α radiation to identify the crystalline phases present. Differential thermal analysis (DTA) and thermogravimetry (TG)

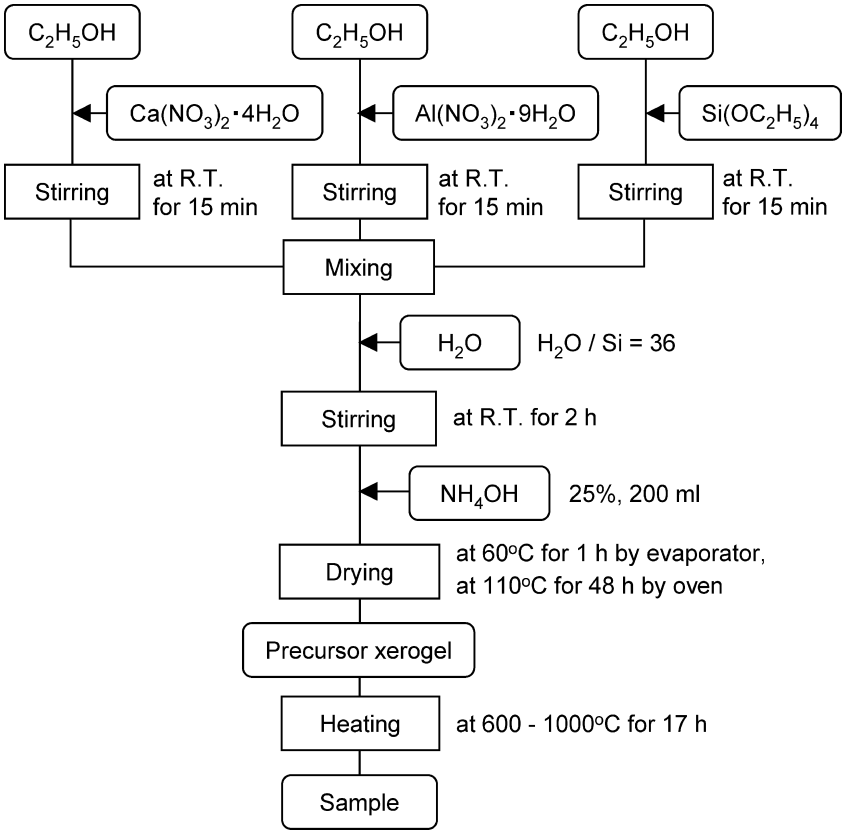

Fig. 1. Experimental flow chart for sample preparation.